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# The effect of electrolytes on emulsions stabilized by nonionic surfactants

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# The effect of electrolytes on emulsions stabilized by nonionic surfactants

Proefschrift
ter verkrijging van de graad van
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op gezag van de rector magnificus,
dr. C.C. Oosterlee,
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STELLINGEN

1. Permeatiemetingen van Zeman aan hydrofobe ultrafiltratie-membranen wijzen uit dat deze membranen hydrofiel genoemd moeten worden.
   Zeman, L.J. (1983), J. Membrane Sci. 15, 213-230.

2. Een beter inzicht in het adsorptiemechanisme van nonionogene zepen zou door Kronberg et al. verkregen zijn, indien zij ook vlokmetingen zouden hebben uitgevoerd.
   Kronberg, B., Stenius, P. en Thorssell, Y. (1984), Colloids and Surfaces 12, 113-123.

3. De resultaten van Teo et al. geven aanleiding tot een systematisch onderzoek naar de faktoren die bepalend zijn voor de molekuulgrootte van geëthoxyleerde nonionogene zepen aan een oppervlak.
   Teo, H.H., Yeates, S.G., Price, C. en Booth, C. (1984), J.C.S. Faraday Trans.I 80, 1787-1794.
   Dit proefschrift, hoofdstuk 3.

4. De resultaten van Suzuki et al. over de aggregatietoestand en de oppervlakteaktiviteit van gemodificeerde immunoglobulinen zijn, in tegenstelling tot wat zijzelf beweren, wel konsistent met elkaar.
   Suzuki, T., Kanbara, N., Tomono, T., Hayashi, N. en Shinohara, I. (1984), BBA 778, 248-255.

5. De resultaten van Furusawa et al. betreffende de plateauadsorpties en hydrodynamische laagdikten als funktie van de molekuulmassa voor poly-L-lysine geadsorbeerd aan polystyreen (latex) bij pH 11 laten ook andere interpretaties toe dan in termen van grotendeels recht opstaande helix staafjes.
   Furusawa, K., Kanesaka, M. en Yamashita, S. (1984), J. Colloid Interface Sci. 99, 341-348.

6. Het micelmodel van Ben-Shaul et al. zou realistischer zijn, indien de penetratie van oplosmiddelmolekulen in het micel

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WOORD VOORAF

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LIST OF SYMBOLS

| | |
|---|---|
| $a$ | exponent in the Mark-Houwink-Sakurada equation |
| $a$ | length of the major semi-axis in fig. 3.18 |
| $a_B$ | numerical constant in eq. 3.29 |
| $a_P$ | average number of ethylene oxide units per chain in eq. 2.1 |
| $a_T$ | numerical constant in eq. 3.3 |
| $A$ | surface area |
| $A_{11}$ | Hamaker constant |
| $A_{c,s}$ | numerical constant in eq. 3.23 |
| $A_r$ | relative absorbance |
| $A_{v,s}$ | numerical constant in eq. 3.18 |
| $b$ | length of the minor semi-axis in fig. 3.18 |
| $b_B$ | numerical constant in eq. 3.29 |
| $b_P$ | average additive number of ethylene oxide units per chain in eq. 2.3 |
| $b_T$ | numerical constant in eq. 3.3 |
| $B_2$ | second virial coefficient in eq. 3.25 |
| $c$ | concentration |
| $c_2$ | equilibrium concentration |
| $c_p$ | specific heat capacity of a solution |
| $c_{p,o}$ | specific heat capacity of a reference solvent |
| $c'_p$ | specific heat capacity of a ternary system. |
| $c'_{p,o}$ | specific heat capacity of a binary reference system |
| $\bar{c}^o_{p,SM}$ | standard partial molal heat capacity of a surfactant in the micellar state |
| $c_S$ | relative standard deviation of the surface weighted distribution |
| $c_T$ | numerical constant in eq. 3.4 |
| $c'_T$ | numerical constant in eq. 3.4a |
| $C_o$ | numerical constant in eq. 3.40 |
| $C_1$ | numerical constant in eq. 3.40 |
| $C_M$ | constant, defined in eq. 3.38 |

| | |
|---|---|
| $C_p$(config.) | configurational heat capacity |
| d | liquid film thickness |
| d' | diameter of a droplet |
| $d_e$ | equilibrium liquid film thickness |
| $d'_{eff}$ | effective particle diameter |
| $d_i$ | thickness of layer i (i = 1,2,3.....EO, PO, water...) |
| $d_T$ | numerical constant in eq. 3.4 |
| $d'_T$ | numerical constant in eq. 3.4a |
| $d'_{vs}$ | volume-surface average diameter |
| $\Delta d_i$ | correction to be applied to the equivalent water thickness of layer i |
| $\Delta d_T$ | total correction to be applied to the total equivalent water thickness |
| D | diffusion coefficient |
| $D_c$ | diameter of a cylinder |
| e | elementary charge |
| $f_c$ | numerical constant in eq. 3.15 |
| $f_m$ | activity constant |
| $f_c^u$ | Cabannes factor |
| g | gravitational constant |
| $G_A$ | Van-der-Waals attraction energy |
| $G_{Int}$ | interaction energy |
| $G_S$ | steric repulsion energy |
| h | thickness of the liquid film between two emulsion droplets |
| $\langle h^2 \rangle$ | perturbed root mean square end-to-end distance |
| $\langle h_o^2 \rangle$ | unperturbed root mean square end-to-end distance |
| H | Debye light scattering coefficient defined in eq. 3.26 |
| $i_{90}$ | scattered light intensity at 90° |
| I | ionic strength |
| $I_{ft}$ | numerical constant in eq. 5.15 |
| $I_o$ | intensity of the incident light beam |
| $I_R$ | intensity of the reflected light beam |
| $I_S$ | reflected intensity from the silvery film |

| | |
|---|---|
| $k_A$ | numerical constant in eq. 3.6 |
| $k_B$ | Boltzmann constant |
| $k_c$ | coalescence rate |
| $k_H$ | Huggins constant |
| $k_L$ | numerical constant in eq. 3.27 |
| K | Mark-Houwink-Sakurada constant |
| $K_e$ | equilibrium constant |
| $K_o$ | viscometric polymer constant, defined in eq. 3.33 |
| $K_p$ | partition coefficient |
| l | height difference between part of the liquid film under consideration and the surface of the bulk solution |
| L | constant in eq. 2.4 |
| m | aggregation number |
| m | molality |
| $m_{LS}$ | aggregation number obtained by light scattering |
| $m_{PO}$ | number of propylene oxide units |
| $m_s$ | surfactant molality |
| $m_{ST}$ | aggregation number obtained by surface tension |
| M | molecular mass |
| $M_e$ | molecular mass of the electrolyte |
| $M_{EO}$ | molecular mass of the ethoxy part of the surfactant |
| $M_n$ | number average molecular mass |
| $M_s$ | molecular mass of the surfactant |
| $M_v$ | viscometric average molecular mass |
| $M_w$ | weight average molecular mass |
| $M_{wa}$ | molecular mass of water |
| n | -d(log O.D.)/d(log λ) in fig. 4.9 |
| n | refractive index |
| $n_c$ | number of hydrocarbon groups |
| $n_{EO}$ | number of ethylene oxide units |
| $n_f$ | refractive index film material |
| $n_i$ | refractive index of layer i (i = 1,2,3...) |
| $n_o$ | refractive index of air |

| | |
|---|---|
| $n_s$ | refractive index of solvent |
| $N_{Av}$ | Avogadro's number |
| $N_t$ | total number of emulsion droplets per unit volume |
| $N_o$ | number of emulsion droplets per unit volume at t = o |
| $N_x$ | number of emulsion droplets per unit volume at t = x |
| p | coincidence correction factor |
| $P_D$ | disjoining pressure |
| $P_{EA}$ | external applied pressure |
| $P_H$ | hydrostatic pressure |
| $q_1$ | number of atoms per unit volume |
| r | Fresnel coefficient |
| $r_{11}$ | distance between centres of two atoms |
| R | gas constant |
| $R_1$ | length of the axis of the poly propylene oxide sheet in fig. 3.18 |
| $R_2$ | length of the axis of the outer poly ethylene oxide mantle in fig. 3.18 |
| $R_{11}$ | length of a deformed coil parallel to the axis of the cylinder |
| $R_c$ | ratio of dispersed oil volume and original oil volume |
| $R_H$ | effective hydrodynamic radius of a micelle |
| $R_{HC}$ | effective hydrodynamic radius of the hydrophobic core of a micelle |
| $R_i$ | fraction of light reflected by a liquid film |
| $\langle s^2 \rangle$ | radius of gyration |
| $\langle s_o^2 \rangle$ | unperturbed radius of gyration |
| $S_{ft}$ | numerical constant in eq. 5.15 |
| $S_n$ | n-th moment of a distribution |
| t | time |
| T | temperature |
| U | uniformity coefficient |
| V | volume |
| $V_1$ | molar volume of the solvent |

| | |
|---|---|
| $V_h$ | hydrodynamic volume |
| $\bar{V}_p$ | partial specific volume of polymer |
| $\bar{V}_S^o$ | standard partial molar volume of the surfactant |
| $\bar{V}_{S,M}^o$ | standard partial molar volume of the surfactant in the micelle |
| $\bar{V}_{S,S}^o$ | standard partial molar volume of a monomeric surfactant |
| $x_1$ | mole fraction of monomeric surfactants |
| $x_a$ | mole fraction of an additive in a micellar solution (eq. 3.6) |
| $x_e$ | mole fraction of electrolyte in a ternary system |
| $x_i$ | mole fraction of i in a mixed solute |
| $x_m$ | mole fraction of surfactant monomers in aggregates |
| $x_s$ | mole fraction of surfactant in a ternary system |
| $x_T$ | totale mole fraction of surfactant (eq. 3.9) |
| $x_{wa}$ | mole fraction of water in a ternary system |
| z | excluded volume parameter (eq. 3.37) |
| Z | valency |
| | |
| $\alpha$ | angle of incidence |
| $\alpha_h$ | linear expansion factor of the end-to-end distance |
| $\alpha_s$ | linear expansion factor of the radius of gyration |
| $\alpha_\eta$ | linear viscosity expansion factor |
| $\beta$ | angle of refraction |
| $\beta_{11}$ | London dispersion constant |
| $\beta_v$ | numerical constant in equation 3.14 |
| $\gamma$ | surface- or interfacial tension |
| $\gamma_d$ | constant, defined by eq. 5.6b |
| $\Gamma$ | adsorbed amount |
| $\Gamma_m$ | adsorbed amount at complete monolayer coverage |

| | |
|---|---|
| $\delta$ | chemical shift parameter |
| $\Delta$ | phase difference between the light beam reflected at the front and back of a liquid film |
| $\varepsilon$ | molar extinction coefficient |
| $\varepsilon_d$ | dielectric constant |
| $\eta$ | viscosity |
| $[\eta]$ | intrinsic viscosity |
| $\eta_{sp}$ | specific viscosity |
| $[\eta]_\theta$ | intrinsic viscosity at $\theta$ conditions |
| $\theta$ | theta conditions |
| $\kappa$ | reciprocal Debye length |
| $\lambda$ | wavelength |
| $\Lambda_{crit}$ | critical wavelength (eq. 6.5) |
| $\mu^o_{aq}$ | standard chemical potential of a hydrocarbon dissolved in water |
| $\mu^o_{hc}$ | standard chemical potential of a hydrocarbon dissolved in a hydrocarbon solvent |
| $\nu_o$ | number of counterions per unit volume |
| $\xi$ | ordering parameter |
| $\rho$ | density |
| $\rho_o$ | density of a reference solvent |
| $\rho'$ | density of a ternary system |
| $\rho'_o$ | density of a binary reference solvent |
| $\Delta\rho$ | density difference |
| $\rho_u$ | depolarization ratio |
| $\sigma_c$ | heat capacity per unit volume |
| $\sigma_{c,o}$ | heat capacity per unit volume of a reference solvent |
| $\sigma_i$ | molecular area of i |
| $\tau$ | turbidity |
| $\phi$ | volume fraction |
| $\phi_{c,s}$ | apparent molal heat capacity of the surfactant |
| $\phi^o_{c,s}$ | apparent molal heat capacity of the surfactant at infinite dilution |
| $\phi'_{c,s}$ | apparent molal heat capacity of the surfactant in a ternary system |

| | |
|---|---|
| $\phi_{v,s}$ | apparent molal volume of the surfactant |
| $\phi^{o}_{v,s}$ | apparent molal volume of the surfactant at infinite dilution |
| $\phi'_{v,s}$ | apparent molal volume of the surfactant in a ternary system |
| $\Phi_o$ | Flory constant |
| $\chi$ | Flory-Huggins polymer-solvent interaction parameter |
| $\psi_d$ | diffuse double layer potential |
| $\omega$ | vibration period |
| $\omega_o$ | vibration period of a reference solvent |

# 1 INTRODUCTION

## 1.1 General background

Since the last decades the stability of colloidal dispersions has been the subject of many studies. Before and during the Second World War several groups were working simultaneously on a stability theory for electrically stabilized particles. This research ultimately led to the DLVO-theory, named after Derjaguin and Landau (1941) and Verwey and Overbeek (1948), who, independently of each other, solved the main problems. This theory describes the interaction of two particles as the sum of Van-der-Waals attraction and electrostatic repulsion in a quantative way. Destabilization can be attained by lowering the repulsion, which, in turn is effectuated by compressing the diffuse part of the double layer through the addition of electrolyte to the system.

The possibility of stabilization and destabilization by polymers is also known for a long time. However a full theoretical description of these phenomena has still not yet been achieved (Vincent and Whittington, 1980; Tadros, 1982). Two main types of phenomena may be distinguished. In the first place stabilization or destabilization can be achieved by the presence of free polymer in solution. At relatively low polymer concentration destabilization of colloidal dispersions occurs. This is due to depletion of polymers near a surface, which results in an osmotic attraction between two particles when two such depletion layers overlap. At much higher polymer concentration stability arises from depletion of the concentration of polymer between the surfaces of particles when they are in close vicinity. Closer approach of the particles can only be obtained by pushing polymer solution out from between the particels against a concentration gradient. In good solvent this latter process is energetically unfavourable (Asakura and Oosawa, 1958; Sieglaff, 1959; Vrij, 1976; Feigin and Napper, 1980a, b; Fleer *et al.*, 1984).

The second type of stabilization and destabilization can be achieved by polymer adsorbed to the surface. Destabilization of a suspension can be realized by adding a small amount of polymer. This flocculation behaviour can be explained by a bridging mechanism: tails and loops of polymers adsorbed on one particle adsorb onto

uncovered patches of other particles leading to flocculation (LaMer and Healy, 1963; Slater and Kitchener, 1966; Fleer, 1971). If this process takes place in the absence of electrolyte it is known as "*adsorption flocculation*". In the presence of small amounts of electrolyte the flocculation is enhanced by compression of the diffuse part of the double layers of the particles, in combination with specific adsorption (*sensitisation*) (Fleer, 1971). These destabilization processes are often used in practice, for instance in water purification.

Stabilization of a suspension by polymer adsorption (physically or chemically adsorbed) is called *steric stabilization.* Stability arises from the segmental overlap and loss of conformatial entropy of the adsorbed polymer on the surface (Scheutjens and Fleer, 1982a, 1984). This stabilization phenomenon (sometimes in combination with stabilization by free polymer) is used, in one way or another, in many branches of industry, like food, paint, pharmaceutical and agriculture industries, and in electronic industry where polymers are used as stabilizers for magnetic "fluids".

Many theoretical problems still remain even about the process of polymer adsorption. Until now a completely rigorous quantitative theory is still lacking, although the theory of Scheutjens and Fleer (1979, 1980) presents a major step in the right direction. The same theory could also be extended to the problem of interaction of polymers at interfaces (Scheutjens and Fleer, 1984).

In steric stabilization the solvent quality is an important variable. It can be changed by altering the temperature, ionic strength etc. It is noteworthy that many sterically stabilized systems can resist very high electrolyte concentrations. A biological example of this is the occurence of halophilic bacteria in the Dead Sea, where the salt concentration exceeds 5 molar. The steric stabilization in systems with a high electrolyte concentration is also important for technological applications like corrosion prevention, nautical affairs and offshore oil production. Understanding stability in such high electrolyte concentrations is a scientific challenge since the well known stabilization theories, like the DLVO theory are only applicable for much lower electrolyte concentrations.

The stabilization mechanism in systems with a high electrolyte concentration must have a clearly different origin. However there is little theoretical knowledge for the origin of this stability. To gain some insight in these phenomena it may be worthwhile to study the stability in high electrolyte concentration in a systematic manner. For various reasons oil-in-water-emulsions stabilized by oligomeric nonionics of special design were selected for the present investigation.

## 1.2 Systems and outline of this study

"Synperonic NPE 1800" was chosen as the stabilizer. This is an oligomeric nonionic surfactant of the A-B-C-type in which A is a rigid hydrophobic part, B is a flexible block of essentially hydrophobic elements and C is a flexible block of hydrophilic elements. It is a commercial product manufactured by Imperial Chemical Industries (U.K.). This surfactant is know to stabilize effectively various dispersions in saline and is therefore suitable for our purpose. Since a number of important structural properties of this substance are not known, it was necessary to characterize the surfactant. The manufacturer especially prepared some derivatives in which the hydrophilic block was made longer. For comparative purposes in some cases a nonionic surfactant of the A-C-type has also been used. All the materials used were commercial products and used without further purification (chapter 2 and 3).

Although oil-in-water-emulsions were the main object of our study, a few other adsorbents were also investigated. Liquid paraffin was used for the dispersed phase in the emulsions. Since adsorption and flocculation studies (chapter 4) are not easily performed on emulsions, monodisperse polystyrene latex and a pyrogenic silica were included as alternative adsorbents. The adsorbed amount of the nonionic surfactant was followed as a function of molecular weight, temperature and electrolyte concentration. Since the solvent quality for the surfactant is likely to be an important factor determining adsorption, this property is considered in some detail together with the stability against flocculation at various solvent qualities, using different adsorbents stabilized with the same surfactant.

Free liquid films are very good models for studying the factors which play a role in colloidal stability. Therefore measurements were performed with free liquid films stabilized by the same surfactants as used for the coalescence and flocculation experiments. The results of these measurements will be discussed in chapter 5.

Chapter 6 deals with the stability of the oil-in-water-emulsions, stabilized by Synperonic NPE 1800 against coalescence as a function of temperature, nature and concentration of electrolyte, and volume fraction of the disperse phase. We shall demonstrate that coalescence and flocculation of these emulsions depend in a very different way on the electrolyte, supporting the view that these two processes are entirely different phenomena.

Finally in the last chapter all the obtained results will be compared and an integrated interpretation will be presented.

## 1.3 Terminology

In literature some confusion still exists concerning terminology. For that reason the Commission on Colloid and Surface Chemistry of the Division of Physical Chemistry and the Commission on Macromolecular Nomenclature of the Macromoleculair Division of the International Union of Pure and Applied Chemistry (IUPAC, 1972, 1974) proposed definitions and symbols in order to avoid such problems of definition.

These IUPAC definitions will be followed as closely as possible in this thesis. However, some unclear points still remain. For example the emulsifier used in this study has properties of both a nonionic surfactant (as indicated by micelle formation and significant lowering of the interfacial tension) and a block copolymer (as indicated by its length and adsoption characteristics). Both definitions will be used depending on the type of investigation.

Following LaMer (1966) distinction is usually made between flocculation (aggregation due to polymers) and coagulation (aggregation due to double layer compression by electrolytes). In this work the stability results from the presence of the adsorbed nonionic surfactant and destabilization is achieved by changing the solvent quality for the nonionic. This type of aggregation will be referred

to as flocculation even if the solvent quality is reduced by the addition of electrolytes.

The IUPAC definitions make a clear distinction between coalescence and flocculation of an emulsion. Coalescence is the aggregation of droplets with the disappearance of their separate boundaries in contact and the formation of a droplet with a smaller surface area than the sum of the surface areas of the separate droplets. On the other hand, flocculation is only the aggregation of droplets. Therefore, coalescence is an irreversible process whereas flocculation may not be necessarily so.

Another process, which may be related to flocculation of an emulsion, is creaming. According to the IUPAC definitions "creaming is the macroscopic separation of a dilute emulsion into a highly concentrated emulsion, in which interglobular contact is important, and a continuous phase under action of gravity of a centrifugal field. This separation usually occurs upwards, but the term may still be applied if the relative densities of the dispersed and continuous phase are such that the concentrated emulsion settles downward". Creaming is enhanced by flocculation, and since there are more interglobular contacts in the cream, coalescence is promoted by creaming. In literature the distinction between flocculation and coalescence is sometimes not strictly followed (Reddy *et al.*, 1981). However in the present thesis this distinction will be clearly maintained.

# 2 STRUCTURAL CHARACTERIZATION OF SYNPERONIC SURFACTANTS

## 2.1 Introduction

The main part of this study has been carried out using a nonionic surfactant composed of *nonylphenol*, *polyoxypropylene* and *polyoxyethylene*, made by ICI-Petrochemical and Plastics Division and sold under the name *Synperonic NPE 1800*. Some work has been done using three other derivatises, namely *NPE A*, *NPE B* and *NPE C*. The four surfactants differ only in the amount of ethylene oxide. For comparison purposes some experiments have been carried out with a second series of ethoxylated nonyl-phenols which will be referred to as the Synperonic NP series. Throughout this work we will use the abbreviation NPE to denote the first series and NP to refer to the second series. The general structural formulas are given in fig. 2.1. In the present chapter the synthesis, properties and characterization of these surfactants will be described.

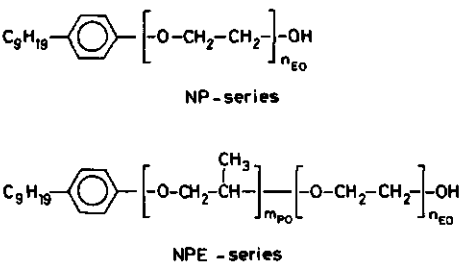


Fig. 2.1 General formulas of Synperonic surfactants.

## 2.2 Synthesis

Nonylphenol is synthesised by reacting nonene with phenol at 343 K with boron trifluoride as the catalyst (Enyeart, 1967). The reac-

tion conditions can be optimised in such a way that the yield is more than 90% monononylphenol with the nonylgroup in the para position. By distillation the pure para compound can be obtained. It should be stressed that this purity does not mean that the nonylgroup is unbranched; this depends to a large extent on the starting material.

The most common process of addition of ethylene oxide (or propylene oxide) to a hydrophobic compound is by condensation. This reaction takes place under basic conditions by adding ethylene oxide to an alkylphenol following a second order nucleophilic substitution (fig. 2.2, Shachat and Greenwald, 1967). The over-all reaction consists of two steps.

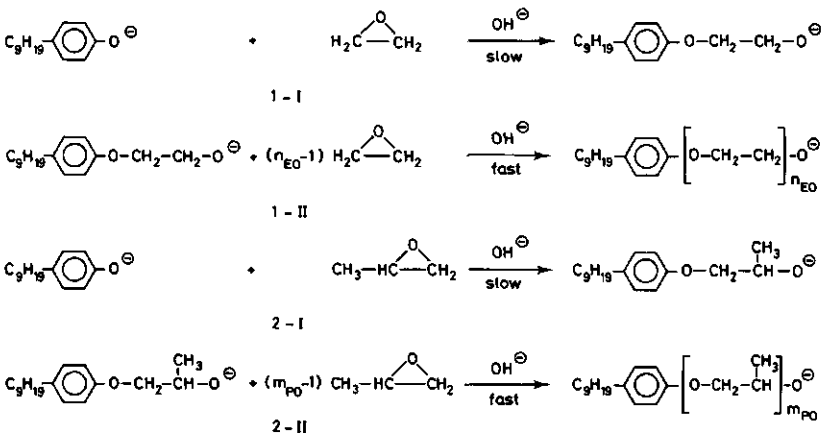


Fig. 2.2 Mechanism of ethylene oxide(1)- and propylene oxide(2)-condensation.

First, addition of ethylene oxide to the alkylphenol takes place to give the monoadduct, followed by subsequent addition of ethylene oxide in a polymerization reaction, at a much higher rate.

Propylene oxide is attacked predominantly at the least substituted ring carbon-atom (reaction mechanisms 2-I and 2-II in fig. 2.2). There are no termination reactions. Polymerization continues until all ethylene oxide has reacted or until the base is neutralized. The end-product will consist of a mixture of ethoxylated alkylphenols with various numbers of ethoxy groups. The polymerization reaction leads to a Poisson distribution (Flory, 1940; Weibull and Nycander, 1954; Tischbirek, 1960). If the degree of polymerization is not too high ($n_{EO} \leq 20$) the various compounds can be separated by means of modern chromatografic methods (Otsuhi and Shiraishi, 1979).

A completely different way of synthesizing polyoxyethylene adducts has been described by Mulley (1967). This method is an extension of the synthesis of simple ethers (Williamson synthesis). With the help of this technique it is possible to synthesize compounds with a degree of ethoxylation of about 20. The advantage of this method is the much easier fractionation with a relatively high yield (Mansfield and Locke, 1964; Robson and Dennis, 1978). With an improved way of synthesizing ethylene glycol oligomers with a relatively high number of ethylene oxide groups (Marshall *et al.*, 1980), it should probably be possible to obtain in the near future pure ethylene oxide adducts with an even higher number of ethylene oxide groups.

## 2.3 Properties

The melting point of all Synperonics increases with increasing number of ethylene oxide groups. No systhematic study has been carried out on the effect of propylene oxide groups built in the molecule on the physical properties of the surfactants. However some information may be derived from the data of Schmolka (1967). These suggest that the melting point is lowered by the presence of a few propylene oxide groups. This trend is also reflected in the physical appearance of the Synperonic surfactants at room temperature. Synperonic NP with a low degree of ethoxylation is a liquid, surfactants with a degree of ethoxylation of about 15 are pastes and above about 20 the surfactants are solids. However Synperonic NPE 1800 with about 26 ethylene oxide groups is a paste

at room temperature. The higher Synperonic NPE's are solids. The solution properties will be discussed in chapter 3.

An important reason for the wide application of ethoxylated surfactants is their biodegradability with respect to their ethylene oxide part (Schick, 1967). It is therefore necessary to pay attention in some respect to the chemical and physical stability of the surfactants during the time of experiments. In literature much attention has been paid to the degradation of poly ethylene oxide itself. Augustyniak and Wojtczak (1980) showed that poly (ethylene glycol) in aqueous solution degrades under influence of irradiation only in the presence of small amounts of intentionally added sensitizers. Mitchell *et al.* (1983) reported no changes in the physical properties of samples stored below 273 K for more than 10 years. The NPE samples described here have been stored in the dark at room temperature. During this study no changes in properties have been observed. The Synperonic NP series were obtained at a late stage of this study and have been stored in the same way. To reduce any degradation small amounts (< 1 mMol) of the bactericide sodiumazide were added provided such addition did not interfere with the experiments. As further precaution all solutions were kept in the dark. Moreover most experiments were performed with freshly prepared solutions.

## 2.4 Characterization

### 2.4.1 Characterization using proton magnetic resonance

In general information about the structure of molecules can be obtained from *nuclear magnetic resonance* (nmr). In these experiments the sample under investigation, containing magnetic nuclei is placed between the poles of a strong magnet. In this case the protons of the sample were used as magnetic probes, the so-called *proton magnetic resonance* (pmr) technique. The protons react with the applied external magnetic field and with the magnetic field caused by the surrounding nuclei. Protons in different parts of a molecule, or belonging to different molecular conformations, experience different total fields and require a slightly different external field to reach resonance. An useful parameter is the

coupling constant which is a measure for a separation of the resonance signal due to nuclear spin-spin interaction between protons attached to adjacent carbon atoms. The amount of resonance is proportional to the number of protons (Carrington and McLachlan, 1967).

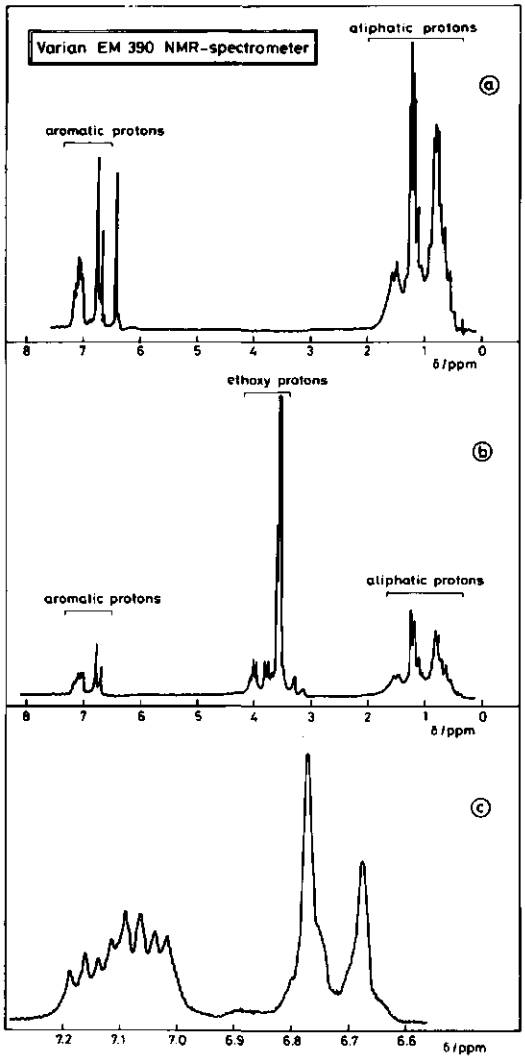


Fig. 2.3 Pmr-spectra of nonyphenol (a), Synperonic NP 4 (b) and an enlarged part of the aromatic protons signal (c).

Thus, when this technique is applied to the Synperonic surfactants an estimate can be obtained of the ratio between the average number of protons from the ethylene oxide groups and the aliphatic and aromatic protons. Accurate results can be obtained with surfactants containing a small number of ethylene oxide groups. Therefore the NP surfactants will be considered first.

The pmr-spectra of nonylphenol and Synperonic NP 4 are given in figs 2.3.a and b respectively. The difference between these two spectra is caused by the protons of the ethylene oxide groups and by the chemical shift of the alcohol proton due to different nuclear environments. The four aromatic protons exhibit a resonance at low field ($\delta$ = 7 ppm) and the resonance at high field ($\delta$ = 0.5 - 1.5 ppm) originates from the aliphatic protons of the nonylgroup.

The shape of the aromatic curve (fig. 2.3.c) is not easily accounted for. By virtue of the reaction mechanism a para substitution should have been expected, giving rise to pmr-spectrum as schematically is represented in fig. 2.4.a. The experimental spectrum does not resemble the theoretical one, neither in the case of a meta nor of an ortho substitution (see fig. 2.4.b and c). Closer examination of the experimental spectrum shows that the areas of the left and right part are equal. Moreover, all the coupling

Table 2.1 Average number of ethylene oxide groups of Synperonic NP surfactants obtained by pmr-measurements

| Surfactant | $\bar{n}_{EO}$(pmr) |
|---|---|
| NP 4 | 3.9 |
| NP 8 | 7.9 |
| NP 9 | 9.0 |
| NP 10 | 10.1 |
| NP 12 | 12.0 |
| NP 15 | 15.8 |
| NP 20 | 22.0 |
| NP 30 | 22.7 |

constants of the left part appear to be equal to each other and the chemical shift in total corresponds almost entirely to a para substitution. All of this suggests a composite aromatic resonance signal belonging to a mixture of four differently branched alkylphenols with a substitution on the para position (fig. 2.4.d). After comparison of the aromatic resonance signal before and after ethoxylation it can be concluded that there is no significant preference for any of these aliphatic nonyl isomers.

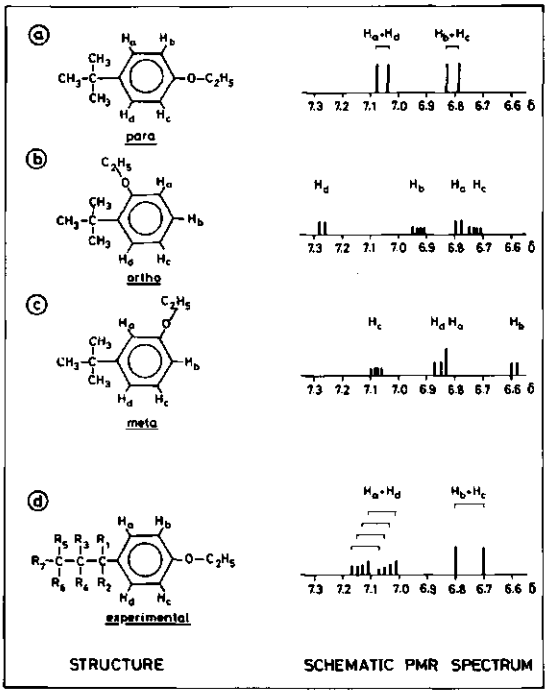


Fig. 2.4 Comparison between schematic pmr spectra of para-, ortho- and meta-t-butyl ethoxybenzene (fig. a, b and c respectively) and the obtained experimental spectrum of nonyl ethoxybenzene (d) (see text) (only the ortho-coupling is included).

Using pmr the number of ethylene oxide groups for different Synperonic NP's have been obtained. The results are given in table 2.1. It is clear that there is discrepancy between the determined number of ethylene oxide groups ($n_{EO}$) and those quoted by the manufacturer above $n_{EO}$=20. This has been reported before for other ethoxylated surfactants (Kayes and Rawlins, 1979). The same problem arises with Synperonic NPE due to the still higher number of ethoxy groups. However a reasonable estimate can be made of the number ratio of ethylene oxide and propylene oxide groups by considering the resonances of the aliphatic protons. With the help of these an attempt has been made to estimate the absolute numbers of the two kinds of oxide groups, taking into account that the absolute amount of propylene oxide should be equal for the four different surfactants (Hancock, 1981). The results, which are obviously much less reliable than the ones obtained for the NP surfactants are given in table 2.2 with the corresponding molecular masses. The indicated errors are standard deviations derived from several different pmr-experiments.

Table 2.2 Average numbers of ethylene oxide groups ($n_{EO}$) and propylene oxide groups ($m_{PO}$) of Synperonic NPE surfactants obtained by pmr-measurements and the corresponding molecular masses.

| Surfactant | $\bar{m}_{PO}$ | $\bar{n}_{EO}$ | M (kg mol$^{-1}$) |
|---|---|---|---|
| NPE 1800 | 12.9 ± 2.2 | 27.5 ± 3.4 | 2.18 ± 0.28 |
| NPE A | 12.9 ± 2.2 | 48.0 ± 5.0 | 3.08 ± 0.35 |
| NPE B | 12.9 ± 2.2 | 79.4 ± 8.6 | 4.46 ± 0.51 |
| NPE C | 12.9 ± 2.2 | 174.2 ± 19.4 | 8.65 ± 0.98 |

## 2.4.2 Characterization using chromatography

As mentioned above the ethyleneoxide condensation method leads to a Poisson distribution of the reaction products (Flory, 1940; Shachat and Greenwald, 1967). Weibull and Nycander (1954) found for ethoxylated adducts that the Poisson distribution is applicable for ($n_{EO}$-1) substituted ethoxy groups. This has been confirmed experimentally in the case of ethoxylation with various chromatographic techniques like thin layer chromatography (tlc) (Robson and Dennis, 1978; El Seoud *et al.*, 1981) or gel permeation chromatography (gpc) (Bombaugh, 1970; Ishiguro *et al.*, 1982).

In the present study two different types of gas chromatography-mass spectrometry combined analyses (gc-ms) have been performed. The first analysis was attempted to verify if the nonylphenol contained admixtures (preceding section). A gas chromatogram of nonylphenol in methanol at 483 K is shown in fig. 2.5. By means of mass spectrometry it could be shown that the different peaks originated from about 12 of the theoretical 167 isomers of nonylphenol.

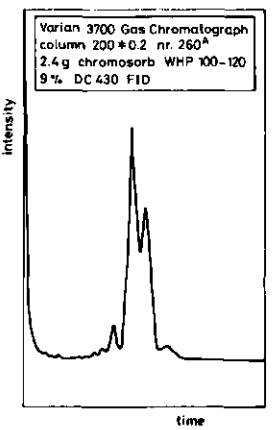


Fig. 2.5 Gas chromatogram of nonyl-phenol in methanol at T = 483 K

In the second analysis the distribution of the surfactant with the smallest number of ethylene oxide units was unravelled. A

modified Poisson distribution of chain lengths should be expected. Gas chromatography of Synperonic NP 4 was performed at a constant temperature. The curve obtained in this way satisfied Martins equation indicating a homologeous series (Martin, 1949; Walraven, 1968; Karcher *et al.*, 1973. Fig. 2.6). By means of gc-ms the homologues could be ascribed to nonylphenols with an increasing degree of ethoxylation. With this knowledge a quantitative estimate of the homologues could be determined from the gas chromatogram using the analoguous argument of Nadeau *et al.* (1964). The results for the Synperonic NP 4 are represented in fig. 2.7 together with a modified Poisson distribution according to Weibull and Nycander (1954). The agreement is satisfactory and it harmonizes with the unpublished gpc-results of other Synperonic NP surfactants with a larger number of ethoxy groups (Hancock, 1981). By virtue of these results it can be concluded that Synperonic NP has been prepared by condensation. Synperonic NPE must be assumed to be synthesised in a similar way, but unfortunately this could not be verified by these types of experiments.

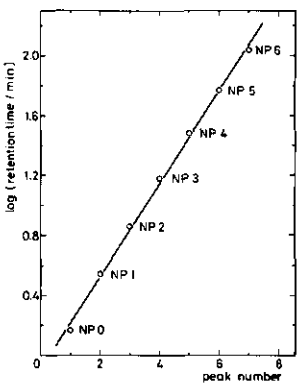


Fig. 2.6 Martins plot of Synperonic NP 4

### 2.4.3 Characterization using ultra violet spectroscopy

Due to the presence of an aromatic ring which gives absorbance in the ultra violet (uv) region of the spectrum, uv-spectroscopy can be applied to characterize Synperonic surfactants. The concentration can be determined using Lambert-Beer's law. Alternatively, uv-spectroscopy can be used to determine the number average molecular mass if the molar extinction coefficient ($\varepsilon$) is known in a certain solvent. Kelly and Greenwald (1958) showed that the molar extinction coefficient was the same for homologous surfactants with different number of ethoxy groups.

Unfortunately, there is no unanimous value known in literature for these surfactants. The $\varepsilon$-value of homogeneous and therefore pure surfactants either has not been properly measured (Mansfield and Locke, 1964) or has not been quoted (Robson and Dennis, 1978). Most quoted literature data have been derived from the values given by Kelly and Greenwald (1958). They measured $\varepsilon$-values of a commercial ethoxylated octylphenol in different solvents and found $\varepsilon$ = 1330 in water at $\lambda$ = 275.5 nm. However Gratzer and Beaven quoted a value of $\varepsilon$ = 1670 in water at $\lambda$ = 278 nm.

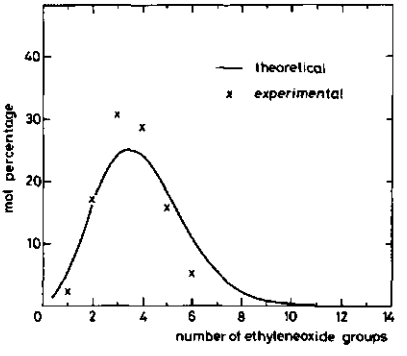


Fig. 2.7 Distribution curve of Synperonic NP 4. Comparison between theoretical modified Poisson distribution and experimental results obtained by gas chromatography.

Because of the confusion with respect to these values we decided to determine the molar extinction coefficient for a NP surfactant series. Due to the aggregation behaviour and limited solubility of the low molecular mass components in water, $\varepsilon$ of different Synperonic surfactants have first been determined in methanol at $\lambda$ = 276.5 nm (table 2.3). The average molecular mass has been used for the calculations. The average value determined in this way conforms very well to the one of Nadeau and Siggia (1967) ($\varepsilon = 1.57 \times 10^3$) for ethoxylated octylphenol surfactants in the same solvent. The data of tabel 2.3 confirm the conclusion of Kelly and Greenwald (1958) that $\varepsilon$ is independent of the number of ethoxy groups. It seems justified to assume that $\varepsilon$ is also independent on the number of propoxy groups. Therefore the number average molecular mass of Synperonic NPE has been determined using the same molar extinction value (tabel 2.4).

Table 2.3 Molar extinction coefficients of some Synperonic NP in methanol at $\lambda$ = 276.5 nm

| Surfactant | $\varepsilon$ |
|---|---|
| NP 4 | 1550 |
| NP 6 | 1559 |
| NP 10 | 1555 |
| NP 12 | 1630 |
| NP 15 | 1599 |
| NP 20 | 1619 |
| NP 30 | 1577 |
| NP $\bar{x}$ | 1590 ± 12 |

Table 2.4 Number average molecular masses of Synperonic NPE surfactants obtained by uv-absorption measurements in methanol at $\lambda$ = 276.5 nm

| Surfactant | M ($kg\ mol^{-1}$) |
|---|---|
| NPE 1800 | 2.150 ± 0.016 |
| NPE A | 3.154 ± 0.023 |
| NPE B | 4.730 ± 0.034 |
| NPE C | 9.334 ± 0.068 |

Since all other experiments were performed in water, the uv-behaviour of the surfactants has also been studied in this solvent. It is known that in water surfactants can aggregate above a certain concentration, which is characteristic for each surfactant, namely the *critical micelle concentration* (c.m.c.) (see next chapter). This association of surfactants induces a shift of the uv-absorption maximum towards a larger wavelength, because the chromophore finds itself in a more apolar environment (Luck, 1960; Gratzer and Beaven, 1969). Consequently at a fixed wavelength the linear relationship between extinction and concentration following Lambert-Beer's law may not be observed. Indeed a deviation from linearity has been measured for the Synperonic NP around the c.m.c. At $\lambda$ = 276.5 nm $\varepsilon$ was 1.33 x $10^3$ below the c.m.c. and 1.64 x $10^3$ above the c.m.c. This difference may account for the established discrepancy in the literature values.

Because of the extremely low c.m.c. values of Synperonic NPE no uv adsorption can be detected below that concentration and therefore it suffices to use the value for c > c.m.c.

## 2.5 Molecular mass distribution

In section 2.4.2 experimental evidence has been given showing that Synperonic NP 4 satisfied a modified Poisson distribution. It was also stated that it was reasonable to assume that both Synperonic NP surfactants and NPE surfactants have been manufactured following a condensation reaction.

However, Synperonic NPE A, B and C have been obtained by a single, two-fold, and three-fold ethoxylation respectively, starting from Synperonic NPE 1800 (Hancock, 1981). This latter surfactant is a block co-surfactant, with a block propylene oxide in the centre of the molecule, between the nonylphenolgroup and the ethylene oxide group and the ethylene oxide block (Van den Boomgaard *et al.*, 1983) (see fig. 2.1.b).

In spite of this (k+1)-fold ethoxylation it can easily be shown that single Poisson-distribution of the molecular mass persists. This will be demonstrated here for a two-fold ethoxylation, but which can easily extended to higher values of k.

For ethoxy chains prepared by a single condensation reaction the number average molecular mass obeys the relationship:

$$M_n = \frac{\sum_i \left[\frac{e^{-a_p} a_p^i}{i!} \cdot i \cdot M\right]}{\sum_i \frac{e^{-a_p} a_p^i}{i!}} = \frac{\sum_i [f(i) \cdot i \cdot M]}{\sum_i f(i)} \qquad (2.1)$$

Where M is the molecular mass of an ethoxy unit, i is an integer and $a_p$ is the average number of ethylene oxide units per chain. The denominator of equation 2.1 equals one.
If such a distribution undergoes a second ethoxylation one obtains the following number average molecular mass:

$$M_n = \frac{\sum_{ij} f(i) \cdot g(j) \cdot [i+j] \cdot M}{\sum f(i) \cdot g(j)} \qquad (2.2)$$

with

$$g(j) = \frac{e^{-b_p} b_p^j}{j!} \qquad (2.3)$$

where j is an integer and $b_p$ is the average additive number of ethylene oxide units. If a part of this overall distribution is considered at which the number of ethylene oxide units have a constant value (L), this can be written as:

$$h(L)\cdot L\cdot M = e^{-(a_p+b_p)} \cdot (i+j)\cdot M \cdot \sum \frac{a_p^i}{i!} \cdot \frac{b_p^j}{j!} \qquad (2.4)$$

By applying the multinomial formula and dividing by $L\cdot M = (i+j)\cdot M$ this can be rewritten

$$h(L) = \frac{e^{-(a_p+b_p)}}{L!} \cdot (a_p+b_p)^L \qquad (2.5)$$

This can be done for any value of L and therefore a Poisson distribution with L as parameter has been obtained.
This demonstrates clearly that all Synperonic NPE's have the same distribution of the ethoxy molecular mass, independently of the way of ethoxylation.

## 2.6 General discussion

Several analytical techniques exist for characterization of surfactants which unfortunately could not be applied to determine the molecular mass of the Synperonic NPE surfactants. The most common method, the *hydroxy value* determination, could not be applied due to the large number of ethylene oxide units (Hancock, 1981). Determination of the number of oxyalkylene groups by *hydriodic acid clearage* which has been elaborated by Siggia *et al.* (1958) and has been succesfully applied by Barry and El Eini (1976) was not discriminating enough for the used Synperonic NP surfactants. Sometimes *infrared spectroscopy* has been used as an analysis technique for ethoxylated surfactants (Schott, 1964; Nadeau and Siggia, 1967). However for measuring absolute values this technique is only useful after a careful calibration and this technique is only applicable to short ethoxy chains ($n<25$) (Gosa and Donescu, 1979). As both conditions were not fulfilled for the Synperonic surfactants, this method has not been used in this study. Some methods are sensitive to the choice of the solvent. Aggregation of the surfactants may interfere with the analysis in some cases. For instance reasonable values for the molecular mass were impossible to obtain using *vapour pressure osmometry* in water, due to the fact that the number of surfactant monomers in such aggregates

were not known precisely. Using other solvent needs extreme precautions to prevent water absorption which disturbs the measurements. Besides these precautions aggregation behaviour in the solvent should also be known. Due to these problems it was decided not to use this method.

In addition to difficulties with experimental techniques, characterization of the Synperonic NPE surfactants is troublesome because the samples are mixtures of various homologeous specimen. The samples have been considered pure in surface chemical sense because neither did they show a minimum in the surface tension- or interfacial tension-log concentration curve. (see chapter 3)(Rosen, 1981). Although the absence of a minimum is a necessary but not sufficient criterion of purity for surface active agents (Clint, 1975), it was not considerd necessary to select another surfactant.

Fractionation has not been carried out, because in view of the aims of this study, this was not decided necessary. Due to the high degree of ethoxylation, this would not have been easy and would be a study on its own. With the help of chromotographic analysis it is possible to discriminate between surfactants with a degree of ethoxylation of n and n+1 for $n \leq 20$ (Otsuki and Shiraishi, 1979). Chromatography can not only be used for analysis, but also for preparation of homogeneous compounds. However, it is not known if large homogeneous quantities of ethoxylated surfactants can be obtained in this way. These can be obtained by following the Williamson synthesis route (Mansfield and Locke, 1964; Robson and Dennis, 1978; Mitchell *et al.*, 1983).

Considering all these problems consistent results have been obtained by pmr and uv. After determination of the molar extinction coefficient of ethoxylated alkylphenols in methanol, the uv-method has appeared to be the most realible technique with an estimated inaccuracy of less than 1%. On the basis of these data and the ratio of the propylene oxide-ethylene oxide obtained by pmr, the values for $n_{EO}$ and $m_{PO}$, and the molecular masses have been calculated. The results are given in table 2.5 and shall be used throughout this study. These values deviate slightly from earlier published results (Van den Boomgaard *et al.*, 1983). These were however based on a less accurate determination of the molar extinction coefficient.

Table 2.5. Average number of ethylene oxide groups ($n_{EO}$) and propylene oxide groups ($m_{PO}$) of Synperonic NPE surfactants obtained by pmr and uv measurements and their derived molecular mass.

| Surfactant | $\bar{m}_{PO}$ | $\bar{n}_{EO}$ | M (kg mol$^{-1}$) |
|---|---|---|---|
| NPE 1800 | 13 ± 2 | 26 ± 4 | 2.10 ± 0.30 |
| NPE A | 13 ± 2 | 50 ± 2 | 3.20 ± 0.20 |
| NPE B | 13 ± 2 | 85 ± 3 | 4.70 ± 0.25 |
| NPE C | 13 ± 2 | 190 ± 5 | 9.30 ± 0.35 |

## 2.7 Concluding remarks

Structural characterization of Synperonic NPE surfactants has been performed to obtain the molecular mass. Consistent results have been obtained by pmr and uv-spectroscopy. The results are summarized in table 2.5.

It has been demonstrated that the nonylgroup is branched in different ways but no significant preference for any of the possible isomers could be found for ethoxylation. A modified Poisson distribution of ethoxy units has been shown for Synperonic NP. It has been assumed that Synperonic NPE satisfies too a modified Poisson distribution.

# 3 SOLUTION PROPERTIES OF SYNPERONIC SURFACTANTS

## 3.1 Introduction

A surfactant molecule is composed of a *polar hydrophilic* part and a *nonpolar hydrophobic* part. This gives the molecule special solution- and adsorption properties. In aqueous solutions this leads to the well known situation that the polar part is located in the solution, while the non-polar part tries to avoid this aqueous environment by adsorption onto other phases or by self association into various types of aggregates. This latter process has been described for the first time by McBain (1913), who introduced the term *micelle*. Important features of micelles in water are the high aggregation numbers and the effective separation of the hydrophilic and hydrophobic parts. Micelle formation is reflected in the abrupt change in the concentration dependence of a large number of properties at a particular concentration. For this purpose the concept *critical micelle formation concentration* (c.m.c.) has been introduced. This c.m.c. can be easily determined experimentally by measuring these abrupt changes of a large number of physico-chemical properties if plotted as a function of the total surfactant concentration. The c.m.c. data of many surfactants have been compiled by Mukerjee and Mysels (1971) who give a discussion of the relevance of the c.m.c. concept and a critical survey of the different experimental methods. Other aspects of micelle formation have recently been treated thoroughly in several reviews (Mittal 1977, 1979; Lindman and Wennerström, 1980).

In this chapter some attention will be paid to the concept of micelle formation, to the specific experimental methods which are applicable to study the c.m.c. of the Synperonic NPE surfactants, to the results obtained and to some solution properties of aggregated Synperonic NPE surfactants.

## 3.2 Micelle formation

### 3.2.1 Models of micelle formation

Different models and thermodynamic descriptions have been proposed for micelle formation (Shinoda and Hutchinson, 1962; Hall and Pethica, 1967; Tanford, 1973, 1974; Israelachvili *et al.*, 1976; Nagarajan and Ruckenstein, 1979; Eriksson *et al.*, 1981; Mitchell and Ninham, 1981; Rusanov, 1982). In general a distinction can be made between two common approaches, which both give a good description of the concentration dependence of the molecular properties of the surfactants (Wennerström and Lindman, 1979). Although the starting points of these two approaches are different, these are mostly combined in one model (Birdi, 1977).

In the first approach, the *equilibrium model*, micelle formation starts form an equilibrium between monomers and aggregates and is treated in accordance with a chemical equilibrium:

$$mZ_1 \rightleftarrows Z_m \qquad (3.1.)$$

which has an equilibrium constant

$$K_e = (f_m X_m/m)/(f_1 X_1)^m \qquad (3.2)$$

where the f's are activity coefficients (and usually are set equal to unity) and $X_m$ is the mole fraction of monomers in aggregates. In accordance with this model there should be a gradual change between monomers and aggregates. This is supported by experimental evidence (Williams *et al.*, 1955; Persson *et al.*, 1979). Another experimental support of this model is the fact that after micelle formation the concentration of monomers increases steadily with an increase of the total surfactant concentration (Schott, 1964; Elworthy and Mysels, 1966; Tadros, 1980).

According to the second approach, the *phase separation model*, a micellar solution is considered as a pseudo two-phase system where the c.m.c. is the concentration where the system enters the two-phase region. Below the c.m.c. only monomers are present while above the c.m.c. the concentration of non-micellar molecules is constant.

In the equilibrium model there is no fixed c.m.c. However, the use of the c.m.c. as a characteristic of the system is warranted, when there is only a narrow concentration range covering the transition between monomers and full-size micelles. In other words, the c.m.c. is a well-defined property, provided the micelle formation is a cooperative process and the aggregation number is large (Tanford, 1977).

Although there is now general agreement that the equilibrium model provides a correct description of micelle formation, Rusanov (1982) poses that the main arguments against the phase separation model (the c.m.c. is a small concentration range and the chemical potential and concentration of the monomer are not constant above the c.m.c.) are not necessarily correct. His critisism is based on a statistical mechanical argument. A discrete phase transition may be observed only if the newly-formed phase contains a very large number of molecules. This is not the case for small systems among micelles, where there is not a point but a region of phase transition. The argument that above the c.m.c. the monomer concentration does not rise any more with increasing total surfactant concentration does not hold either in Rusanov's view, because the constancy of the chemical potential should apply only to an equilibrium of macroscopic phases with a flat interface. A small phase with a curved surface may be in equilibrium with its surroundings even at variable concentration. Rusanov concludes that both models are consistent which each other and both are supported by experiments.

Both models are usually sufficiently accurate to account for the concentration dependence of the c.m.c., but as changes in micelle size and shape have to be accounted for, refinements of the models are needed. Hall and Pethica (1967) and Rusanov (1982) extended the phase-separation model by using the thermodynamics of small systems. An extension of the equilibrium model led to the multiple equilibrium model (Tanford, 1974; Israelachvili *et al.*, 1976; Nagarajan and Ruckenstein, 1979; Mitchell and Ninham, 1981).

### 3.2.2. Thermodynamic considerations

Depending on the model chosen for micelle formation, the value of the Gibbs free energy of micellization can be derived in terms of

the c.m.c. The temperature coefficient of the c.m.c. provides an estimate of the corresponding enthalpy. In such an analysis it is implicitly supposed that the aggregation number, shape, size and size distribution of the micelles are kept constant (Emerson and Holtzer, 1967; Holtzer and Holtzer, 1974; Meguro *et al.*, 1981). However, these properties depend on the temperature, particularly in the case of nonionic surfactants, as will be explained later. The way in which they are accounted for depends on the model adopted (Hall and Pethica, 1967; Holtzer and Holtzer, 1974; Muller, 1977; Van den Boomgaard *et al.*, 1983). A drawback of these theoretical analyses is that there is hardly any suitable information available on micellar size, - size distribution and - shape to evaluate the different terms involved. This difficulty could be overcome by measuring the enthalpy of micellization directly and by comparing this with theoretical analyses. This enthalpy can be derived from calorimetric measurements. For example Desnoyers *et al.* (1980) measured the apparent and relative molal enthalpies of some ionic surfactants from enthalpies of dilution. They concluded that micellization occurs over a "broad" concentration range and therefore phase separation models give an over-simplified view of micellization. However, this concentration range is not too "broad" to be compatible with Rusanov's concept. Hence these measurements do not discriminate between the two models.

The direct enthalpy measurements become increasingly difficult for systems of progressively lower c.m.c., as is usually the case for nonionics (Corkill *et al.*, 1964). However a.o. Clint and Walker (1975) succeeded in measuring the enthalpy of micelle formation of some nonionics using calorimetry. Their results showed that these values are more or less equal to those obtained from temperature variation of the c.m.c. using a Clausius-Clapeyron type equation. This indicates that the thermodynamic corrections are of minor importance. Muller (1977) discussed how the enthalpy values that are determined from the temperature dependence of the c.m.c. can be related to the enthalpy from model calculations. Using his model he also arrived at the conclusion, that the error in using the Van 't Hoff relation on the temperature dependence of the c.m.c. will be minor.

However, great care should be taken in using the temperature dependence of the c.m.c. to obtain the enthalpy of micellization since there are not many experimental data available and especially not over a wide temperature range. Besides, little is known about the concentration dependence of the enthalpy. Until information becomes available of the dependence of other micellar characteristics on temperature, it seems justified to use the temperature dependence of the c.m.c. to evaluate the thermodynamic quantities.

### 3.2.3 Molecular interactions responsible for micelle formation

Micelle formation can be considered as a compromise between the tendency of water to avoid contact with hydrocarbon tails and the strong affinity of the polar groups to water. A model description of micellar systems should thus include both aspects. The interaction between the hydrophilic part of the surfactant and the solvent, and the interactions involving the non-polar part of the surfactants will be discussed separately in this section.

The thermodynamic driving force for micelle formation is the hydrophobic effect, whereby hydrocarbon parts of the surfactant molecules are expelled from an aqueous environment to minimize the hydrocarbon water interface. Tanford (1973) indicated that the lowering of this hydrophobic Gibbs free energy can be ascribed analogous to lowering of the Gibbs free energy due to dissolution of hydrocarbons in water. The hydrophobic Gibbs free energy is defined as the difference between the standard chemical potential of a hydrocarbon dissolved in a hydrocarbon solvent at infinitive solution ($\mu^\circ_{hc}$) and in water ($\mu^\circ_{aq}$). This view that the core of the micelle is considered as a small fluid drop is supported by spectroscopic relaxation measurements which show that the freedom of motion of the hydrocarbon tails is the same as that of liquid hydrocarbon (Ribeiro and Dennis, 1977).

From accurate measurements of the solubilities of linear alkanes in water (McAuliffe, 1963, 1966) one finds a linear relationship between the difference in standard chemical potential and the number of secondary bound carbon atoms for a homologous series:

$$\mu^{o}_{hc} - \mu^{o}_{aq} = a_T - b_T n_c \qquad (3.3)$$

As shown above the Gibbs free energy of micellization is related to the c.m.c. leading to the following relationship between the c.m.c. and the length of the hydrocarbon tail, where all other variables, such as the nature of headgroup, are kept constant:

$$RT \ln \text{c.m.c.} = \mu^{o}_{micel} - \mu^{o}_{aq} = c_T - d_T n_c \qquad (3.4)$$

This relation has been experimentally verified for different types of surfactants (Tanford, 1973), although the values of the constants in equations 3.3 and 3.4 are not identical due to two main reasons. Firstly it is difficult to define the exact interface between the hydrocarbon liquid interior and the solvent (e.g. one is not sure whether the first or even the second methylene group near the hydrophilic head group may be considered to be part of this hydrocarbon liquid interior). Secondly, the repulsion between the head groups influences the properties of the hydrocarbon interior.

The effect of temperature on the Gibbs free energy of micellization has already been discussed in section 3.2.2. It is also interesting to consider the temperature effect of only the hydrophobic part of the Gibbs free energy of micellization. An estimate of this effect may be obtained from the influence of temperature on the solubility of alkanes, in the same way as described above for the effect of the hydrocarbon chain length. The solubility of alkanes in water decreases with increasing temperature indicating that the transfer of the hydrocarbon from pure hydrocarbon to water is energetically favourable and that the lowering of the Gibbs free energy must result from a large negative entropy change (Tanford, 1973). Morover, the enthalpy change is strongly temperature dependent, indicating a large heat capacity. This can be associated with changes in the state of water molecules brought about by the presence of the dissolved solute molecules.

Most expressions for the total Gibbs free energy of micelle formation were derived for ionic surfactants in order to estimate the electrical contributions (Tanford, 1974; Israelachvili *et al.*, 1976; Nagarajan and Ruckenstein, 1979).

However, since nonionic surfactants give relatively smaller c.m.c. values it can be concluded that the repulsion between the polar head groups is low. This repulsion arises from dipolar or solvation forces resulting from the hydration shells around the ethoxy units.

It seems that these specific solvation effects are more important in nonionic than in other systems, and, therefore, one should try to consider the structural aspects of the solvent in more detail.

The term "structure" of water is somewhat undefined since there is no frozen spatial arrangement of liquid water molecules. However, we are not here concerned with the "structure" of water in absolute terms but rather with the modification of this "structure" when solutes are dissolved in it. To study such structural effects in more detail, a study of the heat capacity is worthwhile (De Visser, 1973). As pointed out by Frank and Wen (1957) the value of the partial molar heat capacity, which is related to the second derivative of the chemical potential of the solute with respect to the temperature, is very sensitive to structural changes. Everett (1957) introduced an "*ordering parameter*" $\xi$ to give an estimate of the amount of "structure" in water which is determined by the configurational entropy. The configurational heat capacity is then given by:

$$C_p\ (\text{config}) = -\ (\delta H/\delta \xi)_{P,T} \cdot (\delta \xi/\delta T)_P \qquad (3.5)$$

The first differential quotient in this equation will be positive since more ordering increases the enthalpy. Unlike Everett we introduce a minus sign on the right hand side of equation 3.5 to account for the fact that $\xi$ is a decreasing function of T. The "structure" of water can be influenced by the addition of some solutes. The water around simple ions is usually strongly "structured", whereas the water "structure" near hydrophobic groups is relatively weak. In amphiphilic surfactants both types of "structuring" occur, and therefore it may be useful to use the heat capacities as a measure of the hydrophobic-hydrophilic balance.

Systematic studies of the effect of the variation in the polar head groups of nonionics on the c.m.c. are rare and most of these have been carried out using mixtures with an average composition.

Schick *et al.* (1962a,b) reported some c.m.c. values of different surfactants as a function of the number of ethylene oxide groups. For surfactants with a branched hydrocarbon chain they found an increase in c.m.c. with an increasing number of ethylene oxide groups, as expected. The same trend has been reported by Hsiao *et al.* (1956), Seng and Sell (1977) and Warr *et al.* (1983). However Stubičar and Petres (1981) reported a reduction of the c.m.c. with increasing number of ethylene oxide groups for surfactants with a fixed hydrocarbon group. The situation is slightly more complex for surfactants with a straight hydrocarbon tail. For a homologous series of ethylene oxide adducts of n-dodecanol an increase in c.m.c. has been found with an increase in the number of ethylene oxide groups, but the reverse trend has been reported for the adducts of n-octadecanol (Schick *et al.*, 1962b). Both opposite trends were reported for the ethylene oxide adducts of n-hexadecanol. Carless *et al.* (1964) and Güveli *et al.* (1982) found a decrease in c.m.c., while Elworthy and MacFarlane (1963) and Barry and El Eini (1976) measured an increase in c.m.c. values with an increase in the numbers of hydrophilic groups. The measurements of Carless *et al.* (1964) and those of Elworthy and MacFarlane (1963) have been performed with homodisperse derivatives, where as the results of Barry and El Eini (1976) and Güveli *et al.* (1982) have been performed with heterodisperse, commercial samples of the same manufacturer.

The difference between the linear and branched hydrocarbon chains could be attributed to a different packing of the molecules in the micelle (Van den Boomgaard *et al.*, 1983). The absolute amount of ethylene oxide could possibly explain the differences in trends observed for the linear hydrocarbon surfactants. Some trends are difficult to explain and need further investigation. Anyway it is not yet possible to obtain a quantitative picture of the interactions of the polar ethylene oxide headgroup.

### 3.2.4 Surfactant-solvent interaction, solubilization and mixed micelle formation

Changes in the solvent can influence the solubility of the surfactant which, in turn, can affect the association behaviour of the surfactants. If the total solubility of a surfactant is low, no

aggregation will occur at all. However, if the monomer solubility increases with temperature, micellization occurs at a certain temperature, leading to a dramatic increase in solubility, since now the surfactant dissolves as micelles. The temperature at which this increase in solubility takes place is referred as *Krafftpoint*. With ethoxylated nonionics the reverse happens: the total solubility of the surfactants decreases with increasing temperature. The point at which the first "phase separation" can be detected is called the *cloud point*, because a solution of ethoxylated nonionics becomes turbid upon raising the temperature. This clouding has been ascribed to partial dehydration of the ether oxygens. The cloud point depends on the length of the ethoxy group and the surfactant concentration. A long polyethylene oxide group has a higher ability to hydrate and therefore it has a higher cloud point (Nakagawa, 1967).

The presence of a third or more components in the surfactant-solvent system can influence the micellar properties considerably. Two different types of interaction may be distinguished. The first type of interaction results from the influence of the added compound on the solvent properties of the medium; we will discuss such effects later. The second type of interaction results from the effect of the additives on the hydrocarbon core of the micelle. Such materials are more soluble in the hydrocarbon core than in the surrounding solvent, a phenomenon that is usually referred to as *solubilization*. Solubilization usually decreases the c.m.c. From thermodynamic analysis of small systems an equation relating the c.m.c. to the mole fraction of the additive may be derived. Such a relationship is analoguous to Henry's law (Hall, 1970, 1972):

$$c.m.c.(x_a) = c.m.c.(x_a = 0) - k_a x_a \qquad (3.6a)$$

where c.m.c. ($x_a = 0$) is the c.m.c. without additive, $x_a$ is the mole fraction of the additive and $k_a$ is a constant depending on the nature of the system. In most cases $k_a x_a$ is low so that:

$$c.m.c.(x_a) \cong c.m.c.\ (x_a = 0) \qquad (3.6b)$$

Incorporation of a surface active solubilizate in a micelle is

similar to the solubilization phenomenon, producing mixed micelles. Using the phase separation model and treating the mixed micelles as an ideal mixture of its pure components, Lange (1953) and Shinoda (1954) independently derived an expression for the c.m.c. of a binary mixture of a homologous pair of ionic surfactants. Similar expressions may be used for mixtures of more than two nonionic surfactants (Lange and Beck, 1973; Clint, 1975):

$$\frac{1}{\text{c.m.c.(mix)}} = \Sigma \frac{x_i}{\text{c.m.c.(i)}} \qquad (3.7)$$

where c.m.c.(mix) is the c.m.c. of the mixture, c.m.c.(i) the c.m.c. of i in a solution of pure i and $x_i$ is the mole fraction of i in the mixed solute. This equation indicates that binary mixtures have a c.m.c. that lies between the values of the pure components, and that the rate of change in c.m.c. with mole fraction is larger for the small mole fraction of the component with the lower c.m.c. If the mixed micelle does not behave as an ideal mixture, e.g. surfactants having different head groups, equation 3.7 is no longer applicable, but should be modified e.g. using regular solution theory (Rubingh, 1979).

Warr *et al.* (1983) applied equation 3.7 to mixtures with more than two components. These authors showed that the variation of the c.m.c. as a function of the average ethoxy chain length of Poisson distributed polydispersed samples is approximately the same as the variation of the c.m.c. of pure nonionic surfactants.

The influence of changing the solvency of the medium for ethoxylated nonionics by addition of electrolytes has been studied by Becher (1962), Schick *et al.* (1962, 1965), Van den Boomgaard *et al.* (1983) and by Schott *et al.* (1984). In general it has been found that the addition of electrolytes lowers the c.m.c. Different interpretations of this phenomenon have been given in literature. Becher (1962) suggested that the ethylene oxide chain exhibits a small positive charge by oxonium ion formation and that lowering of the c.m.c. has an electrostatic origin. Erlander (1970) endorsed the concept of charge on the polyethylene oxide chain. On the other hand, Schick (1964, 1965) explained the decrease of the c.m.c. by addition of electrolyte in terms of a reduction in solvent quality.

The influence of addition of electrolytes may be considered in terms of its effect on the "water structure" (Frank and Evans, 1948) which leads to a change in the hydration of the polyethylene oxide group thus affecting the c.m.c. (Schott *et al.*, 1984). Van den Boomgaard *et al.* (1983) also explained the reduction in c.m.c. at low electrolyte concentration (< 1 M) in terms of reduction in the solvent quality. However at higher electrolyte concentrations (> 1 M) they found an increase in the c.m.c. with an increase in electrolyte concentration. They attributed this to a possible salting-in of the hydrocarbon moiety by reducing hydrophobic association in aqueous solutions by chaotropic ions.

Another factor which can influence the c.m.c. is the pressure. However the latter must exceed very high values before any change can be detected (Nishikido *et al.*, 1980). The effect of pressure on the c.m.c. is beyond the scope of this study and therefore it will not be discussed any further.

### 3.2.5 Size and shape of micelles

As mentioned before the driving force for micelle formation is the tendency for the hydrocarbon chains to avoid contact with the solvent which leads to an increase in entropy but micellization is opposed by the repulsive forces between the head groups. The same features also affect the size and shape of the micelle.

Tanford (1972, 1973) developed a model for the micelle shape in terms of its molecular properties, such as the length and the volume of the apolar chain and the cross sectional area of the polar head groups. This model has been extended by others (e.g. Israelachvili *et al.*, 1976). Using this essentially simple model one can predict that surfactants with two parallel apolar chains tend to form lamellar structures, as has been found for lecithins and that ionic surfactants with one hydrophobic chain form near-spherical micelles.

Although there is general agreement on the basic factors that determine the shape and size of micelles, there is still some controversy on how such combined factors affect each other. The problem is further complicated by the way in which the different

factors are influenced by variation of the solvent quality. The influence of additives like electrolytes on these basic factors is also very complicated. The size and shape of micelles can be studied in different ways, but in some cases different techniques can give different answers, thus making interpretation of the size and shape of micelles more doubtful (Wennerström and Lindman, 1979). The most commonly used method for studying micelle size and shape is static light scattering. However a disadvantage of this classic technique is the necessity to extrapolate to zero micelle concentration, because at appreciable concentration the intermicellar interactions contribute substantially to the light scattering. This means that information on micelle size and shape can only be obtained at a concentration just above the c.m.c. (Anacker, 1970). For ionic micelles an extra complication arises from the negative ion adsorption which means that co-ions do also contribute to the measured turbidity (Huisman, 1964).

A modern light scattering technique, which can be applied to study micelles, is the dynamic light scattering (Mazer *et al.*, 1976, 1977; Barker and Vincent, 1984). In this technique the temporal fluctuations in the intensity of the scattered light are measured. From the autocorrelation function the effective diffusion coefficient can be obtained and this is related to the radius of the micelle by the Stokes-Einstein equation. This method is relatively insensitive to intermicellar interactions, thus providing valuable information at relatively high surfactant concentrations.

A hydrodynamic technique that can be applied to obtain information on micelle size and shape is viscosimetry. The viscosity of a surfactant solution is sensitive to the size and shape of micelles, but the interpretation of the results is difficult. In principle if the viscosity is measured as a function of micellar concentration, a shape and a size factor may be obtained, but one must be cautious, since the average size of the micelle probably increases with increase of the micellar concentration (Van den Boomgaard *et al.*, 1983).

In spite of the difficulties incurred in the interpretation of the results it has been shown that ionic micelles are nearly spherical at low concentrations and in the absence of electrolytes

(Tanford, 1973; Mazer *et al.*, 1977). The same has been reported for nonionic micelles (El Eini *et al.*, 1976).

### 3.2.6 Influence of temperature and addition of electrolytes on size and shape of micelles

The change of the c.m.c. is usually chosen as the characteristic parameter to study the effect of temperature and/or additives upon surfactant solutions, since c.m.c.'s can be easily determined using various techniques (Schick, 1962a). Mostly the variation of c.m.c. with temperature is used to calculate the enthalpy of micellization again assuming that the size and shape remain constant with variation of temperature (section 3.2.2). However, dynamic light scattering of sodium dodecyl sulfate at various temperatures showed a tendency towards formation of larger micelles with decreasing temperature (Mazer *et al.*, 1976). This is consistent with the decreasing solubility of ionic surfactants with decreasing temperature. Using the same argument one should expect that the micelle size of nonionic surfactants increases with increasing temperature due to the reduction of solubility with increasing temperature (section 3.2.4). This has indeed been found in the case of ethoxylated surfactants as measured by static light scattering (Balmbra *et al.*, 1962,1964). However, careful analysis showed that the light scattering data have been partly misinterpreted. The intense light scattering at higher temperatures is probably not due to the formation of large micelles, but rather due to the formation of large aggregates composed of small micelles (secondary aggregation) (Elworthy and MacFarlane, 1963; Attwood, 1968; Tanford *et al.*, 1977; Staples and Tiddy, 1978). Experimental evidence for this secondary aggregation has been confirmed using a nmr relaxation technique by Staples and Tiddy (1978). They explained the aggregation by considering the dehydration of the nonionic surfactants at higher temperatures leading to reduction in the hydration repulsive force between the nonionic micelles. This net attraction between micelles at higher temperatures is also consistent with the incipient phase separation. The difference in behaviour between nonionic and ionic micelles can be explained in terms of difference in the nature of the repulsive force between the two types of

surfactants. With ionic micelles, the electrostatic forces should play a dominant role in determining the micelle size.

The addition of electrolytes shows a similar effect on the micellar size of ionic surfactants. With an increasing electrolyte concentration larger ionic micelles are formed (Mazer *et al.*, 1976; Staples and Tiddy, 1978; Ozeki and Ikeda, 1981; Offen *et al.*, 1981). This increase of micelle size with increase of electrolyte concentration is more significant at lower temperatures. Similar trends are expected to occur with nonionic surfactants with respect to temperature variation. Experimental results on nonionic surfactants, however, are not as comprehensive as with ionic surfactants. The only data available are those using static light scattering measurements (Schick *et al.*, 1962b), which, as explained above, are not sufficiently discriminative to decide whether secondary aggregation of small micelles will occur or whether the micelles will grow. However from cloud point studies it can be shown that addition of electrolytes to nonionic surfactant solutions produces the same effect as increasing the temperature. It is tempting to suggest that addition of electrolytes causes dehydration of the nonionic surfactants, thus leading to secondary aggregation. However, it must be stressed that there is no experimental evidence that supports this hypothesis. It is therefore interesting to study the effects of electrolytes on the behaviour of nonionic surfactants in more detail.

## 3.3 Critical micelle formation

### 3.3.1 Experimental

The critical micelle concentration of surfactants can be determined in many different ways. However many of the techniques that are used for determination of the c.m.c. of ionic surfactants can not be applied to nonionic surfactants; for instance the conductivity and potentiometric titrations. As the c.m.c.'s of nonionic surfactants are in general much lower than those of ionic surfactants, the applied technique must be very sensitive. For that reason some of the recently developed techniques such as nmr- and esr-spectroscopy are not suitable for nonionic surfactants.

The c.m.c.'s of Synperonic NPE series were determined using two methods. The first method is based on the shift in the uv-spectrum of the surfactant, and this has already been discussed in section 2.4.3. However due to the lack of sensitivity the results obtained were not reproducible. The second method is based on measurement of the reduction of the surface- or the interfacial tension as a function of the surfactant concentration, which was sensitive enough for accurate determination of the c.m.c., providing that stringent precautions were taken to avoid contamination with other surface active materials.

The surface tension measurements were carried out using the Wilhelmy plate method. The solution was kept in a double walled container through which water was circulated from a thermostatted bath with an accuracy of 0.1 K. The Pt-plate was carefully cleaned prior to each measurement. For concentrations much lower than the c.m.c. the surface tension was found to decrease slowly with time. This time variation was partly due to the slow establishment of equilibrium at low surfactant concentration and partly due to the evaporation of the solvent. This caused a slow change in the force balance between plate and solvent with time. This drift problem can be avoided through measuring the c.m.c. after a fixed time (Crook *et al.*, 1964). It has been shown that the c.m.c. values obtained in this way were insensitive to the measuring time, provided this time is relatively short (Van den Boomgaard *et al.*, 1983). All data reported here for the surface tension measurements, apply to a measuring time of 5 min. unless otherwise stated. In the case of interfacial tension between water and solvent with a density lower than water (such as liquid paraffin), evaporation of the water phase does not occur, and the interfacial tension will decrease with time reaching a constant value.

The interfacial tension was measured between an aqueous Synperonic NPE solution and liquid paraffin (ex Merck). Liquid paraffin was selected because it was poorly soluble in water and because the Synperonic NPE's would not dissolve in it. Only the liquid paraffin of Merck was judged suitable for this purpose, because it gave

the smallest reduction in interfacial tension against distilled water with time (see fig. 3.1 curve a). However the initial interfacial tension value of 49.0 mN $m^{-1}$ for this paraffin was decreasing by 4.0 mN $m^{-1}$ in 24 hours. Therefore it was decided to remove the surface active impurities. The most suitable method for removing these impurities was to pass the liquid paraffin over a column of granular Fuller's Earth. The latter has been pretreated by roasting for 2 hours at 873 K. After the paraffin had been purified the initial value of the interfacial tension against distilled water was 53.6 mN $m^{-1}$ and decreased by only 0.6 mN $m^{-1}$ in 24 hours (see fig. 3.1 curve b). It was found necessary to clean all the glassware with chromic acid and to keep the purified liquid paraffin in dark glass bottles.

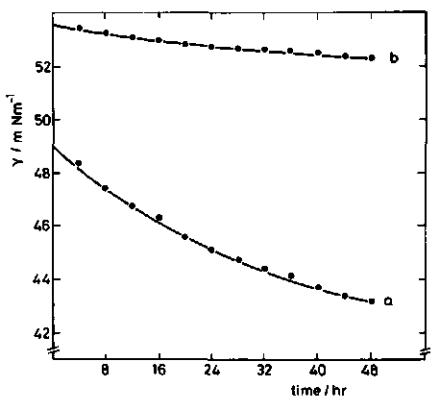


Fig. 3.1 Interfacial tension of liquid paraffin against distilled water at 298 K before (a) and after (b) the liquid paraffin has been purified.

The interfacial tension measurements have been performed with a continuous method. The plate was kept at the interface, while the decreasing interfacial tension was compensated by a force generated by an electronic device. In this way the reproducibility within one measurement was 0.02 mN $m^{-1}$ or better. Corrections were made for the buoyancy of the plate due to its submersion in liquid

paraffin and for the surface tension of the supporting wire at the air-liquid paraffin surface.

Beside obtaining the c.m.c. other valuable information may be obtained from the change of surface tension or interfacial tension with concentration and time. The surface tension can be defined as the increment in Gibbs free energy per unit increment in area. The well known Gibbs equation relates the surface excess of the solute with the rate of reduction of the surface tension with the logarithm of the mole fraction of the solute at constant temperature, for dilute solutions:

$$\Gamma = - \frac{1}{RT} \left( \frac{d\gamma}{d\ln x_T} \right)_T \qquad (3.8)$$

where $\gamma$ is the surface tension or interfacial tension (in mN $m^{-1}$), $\Gamma$ is the surface excess in mole $m^{-2}$, $x_T$ is total mole fraction of surfactant, R is the gas constant and T has its usual meaning. Applying this equation to the equilibrium model (section 3.2.1) Thomas and Christian (1980) showed, that the ratio of the slope before and after the c.m.c. is roughly equal to the micellar aggregation number. This is shown as follows. Assuming the activity coefficient to be equal to 1, the total mole fraction of surfactant ($x_T$) can be related to the mole fraction of monomers ($x_1$), the aggregation number (m) and the equilibrium constant ($K_e$) by the equation:

$$x_T = x_1 + mK_e x_1^m \qquad (3.9)$$

After combining equations 3.8 and 3.9 and after some rearranging, equation (3.8) can be written as:

$$\Gamma = - \frac{1}{RT} \left[ m - (m-1) \frac{x_1}{x_T} \right] \left( \frac{d\gamma}{d\ln x_T} \right)_T \qquad (3.10)$$

If there are no micelles present $x_T = x_1$ and equation 3.10 reduces to equation 3.8. After the c.m.c. has been passed, the mole fraction of the monomers will be so small that the ratio ($x_1/x_T$) is nearly zero and equation 3.10 reduces to:

$$\Gamma = - \frac{m}{RT} \left( \frac{d\gamma}{d\ln x_T} \right)_T \qquad (3.8a)$$

Therefore the ratio of the slope before the c.m.c. to that after the c.m.c. is:

$$\frac{\left(\frac{d\gamma}{d\ln x_T}\right)_{\text{before}}}{\left(\frac{d\gamma}{d\ln x_T}\right)_{\text{after}}} = \frac{- RT\Gamma}{- RT\Gamma/m} = m \qquad (3.11)$$

The value of m, obtained in this way can not be very accurate, but is rather a rough estimate of the aggregation number. With our system, the value obtained for the slope before the c.m.c. was found to depend on the time taken for the measurement (in the case of surface tension), and the variation in the value of the slope beyond the c.m.c. was very large resulting in a large variation in m.

For the case where the reduction of $\gamma$ with time was caused by a diffusion-controlled process, Ward and Tordai (1946) derived for a low-molecular weight compound the following equation:

$$\gamma_0 - \gamma_t = 2ck_BT \sqrt{\frac{D}{\pi}} \cdot \sqrt{t} \qquad (3.12)$$

Where $\gamma_t$ and $\gamma_0$ are the interfacial tension at t=t and t=0 respectively, c is the concentration of the lower molecular weight molecules, $k_B$ is Boltzmann's constant and D the diffusion coefficient. Equation 3.12 applies only at low surface coverage whereby the surfactant molecules diffuse to a nearly empty surface.

### 3.3.2 Results and discussion

Values of the c.m.c. of the Synperonic NPE's at 298 K are given in table 3.1. These values have been obtained from surface tension measurements i.e. at the air-liquid interfaces. The logarithm of the c.m.c. is plotted versus the number of ethoxy groups and the results are shown in fig. 3.2.

Table 3.1 Surface properties of Synperonic NPE at 298 K

| Surfactant | c.m.c. (ppm) | c.m.c. (μM) | Γ (μmol $m^{-2}$) | σ ($nm^2$) | m | π [1] (mN $m^{-1}$) |
|---|---|---|---|---|---|---|
| NPE 1800 | 9.2 | 4.38 | 1.438 | 1.15 | 50 ± 13 | 35.8 |
| NPE A | 15.5 | 4.84 | 1.403 | 1.18 | 30 ± 7 | 33.4 |
| NPE B | 70.7 | 15.0 | 0.750 | 2.22 | 20 ± 5 | 32.0 |
| NPE C | 1310.0 | 140.9 | 0.540 | 3.07 | 8 ± 2 | 30.4 |

1) $\gamma_o$(water) = 72.2 mN $m^{-1}$

The linear dependence of log(c.m.c.) on $n_{EO}$ can be respresented in the following empirical equation:

$$RT \ln(c.m.c.) = c_T' + d_T' n_{EO} \qquad (3.4.a)$$

The experimental values of $c_T'$ and $d_T'$ for Synperonic NPE series show that the effect on lowering of the c.m.c. by elongation of a straight hydrocarbon chain with one $CH_2$-group is outweighed by elongation of the ethylene oxide chain with 5 ethoxy groups. The value of $d_T'$ is somewhat higher than the values collected by Gerrens (1966). However the latter have been obtained for surfactants with ill-defined chain lengths.

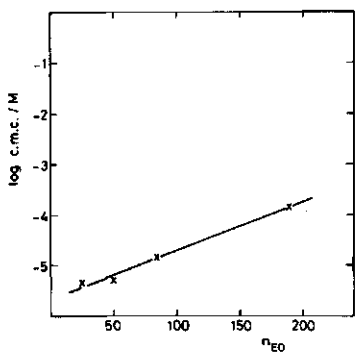


Fig. 3.2 Critical micelle concentrations at 298 K of Synperonic NPE surfactants as a function of the length of the polyoxyethylene moiety

From table 3.1 it is clear that the amount adsorbed decreases with increase of the length of the hydrophilic chain. The same trend was also observed by Barry and El Eini (1976) and Güveli *et al.* (1983). The molecular areas ($\sigma$) of the Synperonic NPE molecules are similar to those obtained with other ethoxylated surfactants with different hydrocarbon moiety, but with roughly the same amount of ethylene oxide (Barry and El Eini, 1976; Güveli *et al.*, 1983). This indicates that the molecular area is determined by the polyoxyethylene chain and not by the nonylphenol and polyoxypropylene groups.

The expected trend for the reduction of aggregation number of nonionic surfactants, with increase in the number of oxyethylene units is also found with the Synperonic NPE series (table 3.1) (El Eini *et al.*, 1976). Increasing the hydrophilic chain length increases the aqueous solubility of the monomer and therefore decreases the driving forces leading to micellization. Moreover as a result of steric hinderance the increase in the flexibility of the polyoxyethylene chains could lead to a decrease in the aggregation number.

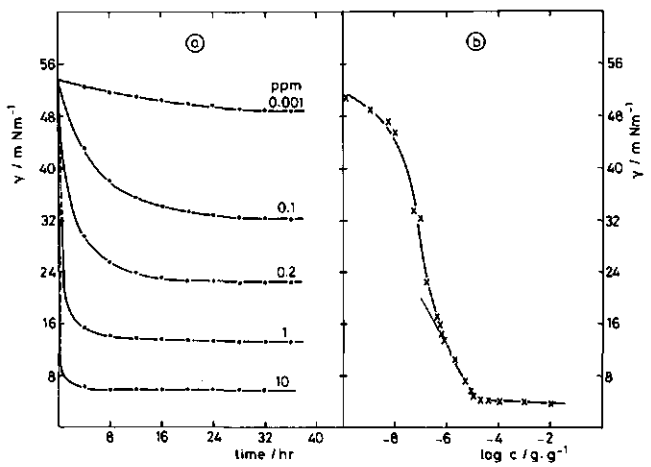


Fig. 3.3 Interfacial tension of aqueous solutions of Synperonic NPE 1800 against liquid paraffin at 298 K as a function of time (a) and as a function of concentration (b).

In fig. 3.3a the interfacial tension of Synperonic NPE 1800 at several concentrations is given as a function of time. From this graph and others (not shown) the limiting values of the interfacial tension are obtained and shown in fig. 3.3b as a function of the surfactant concentration. The related parameters are given in table 3.2.

Table 3.2 Interfacial properties of Synperonic NPE 1800 in different solvents against liquid paraffin at 298 K

| Aqueous solvent | c.m.c. (ppm) | c.m.c. (μM) | Γ (μmol $m^{-2}$) | σ ($nm^2$) | m | π 2) (mN $m^{-1}$) |
|---|---|---|---|---|---|---|
| water | 12.1 | 5.76 | 1.36 | 1.22 | 51 | 49.6 |
| 0.4 M $NA_2SO_4$ | 2.3 | 1.08 | 2.31 | 0.72 | 97 | 50.4 |

2) $\gamma_o$ (water/liquid paraffin) = 53.6 mN $m^{-1}$

Comparison of the data shown in tables 3.1 and 3.2 indicate that, apart from a small difference between the c.m.c. obtained from interfacial and surface tension, all other parameters agree with each other within experimental error.

A rough estimate of the partitioning of the surfactant between the aqueous and the oil phase may be obtained from comparison of the c.m.c. at the oil-water and air-water interface (Crook *et al.*, 1965). For equal volumes of oil and water Crook *et al.* derived the following expression for the partition coefficient:

$$K_p = \frac{\text{c.m.c. (surface tension)}}{\text{c.m.c. (interfacial tension)} - \text{c.m.c. (surface tension)}} \qquad (3.13)$$

If this is applied to the data of Synperonic NPE 1800 this gives a value of 3.2 which is unexpectedly low for a surfactant that is supposed to dissolve in water and not in liquid paraffin. However as mentioned above this is only a rough estimate; a small variation in the logarithm of the concentration can cause a large variation in $K_p$ (in this case this will be in the order of 250 % giving a value of 3.2 ± 8.4).

At low surfactant concentrations the interfacial tension was found to decrease linearly with $t^{\frac{1}{2}}$ (fig. 3.3.a) at low t values and the slope of such a curve ($d\gamma/dt^{\frac{1}{2}}$) is proportional to the surfactant concentration (<0.2 ppm). This is in agreement with the theory of Ward an Tordai (1946) indicating the adsorption process is diffusion controlled. However calculations of the diffusion coefficient (D) from the slope of the line gave very high values for D. Similar results for PVA have been obtained by Lankveld and Lyklema (1968, 1972), who interpreted the data in terms of segments adsorbed instead of whole molecules in equation 3.12. This explanation is not realistic for Synperonic NPE 1800, because this surfactant is a relatively small molecule compared with PVA and it is composed of different blocks, each with a different adsorption energy. At high surfactant concentrations the interfacial tension reaches its final value nearly instantaneously.

The effects of electrolytes and temperature on the c.m.c of Synperonic NPE 1800 have been analyzed by Van den Boomgaard *et al.* (1983). Unfortunately, the data are not sufficiently accurate to obtain the adsorbed amount as a function of electrolyte concentration and temperature. As expected, the c.m.c. decreases with increasing temperature since the solubility of the surfactants decreases as a result of dehydration of the polyethoxy chain. The same interpretation is commonly used to explain the decrease of the c.m.c. with increasing electrolyte concentration. At high concentrations of NaCl Van den Boomgaard *et al.* found an increase in the c.m.c. As mentioned before this has been attributed to a salting-in phenomenon of the hydrocarbon moiety.

Only one experiment has been carried out for interfacial tension measurement in the presence of electrolyte (table 3.2). The results obtained also show a reduction in c.m.c. which is attributed to the lower solubility of the Synperonic in 0.4 M $Na_2SO_4$ as expected.

## 3.4 Volumes and heat capacities

Heat capacity measurements provide a useful method for studying the effect of solutes on the solvent structure (Desnoyers *et al.*, 1980). These measurements can be applied to surfactants in solution. Careful analysis shows that one needs to obtain accurate

measurements below and above the c.m.c.. This is possible with ionic and some nonionic surfactants having a high c.m.c. value. With nonionics such as the Synperonic NPE series having a low c.m.c. value accurate measurements can only be made above the c.m.c. Still such measurements can possibly provide some information about the structure of the surfactant micelles and in particular the effect of solvency e.g. addition of electrolytes. However as we will see later, it appeared that for the Synperonic NPE series such results are difficult to correlate with solution properties.

### 3.4.1 Experimental

The interaction between water and surfactants dissolved in it can be obtained from the thermochemical properties of aqueous surfactant solutions (Desnoyers *et al.*, 1980). These properties can also be used to determine the c.m.c. Unfortunately, most of these techniques have a lower concentration limit of about 0.01 M in water and are therefore unsuitable for nonionic surfactants below the c.m.c. However, these thermodynamic parameters measured far beyond the c.m.c. could still be useful, since they are known to be very sensitive to structural changes in solutions (De Visser *et al.*, 1977; Perron *et al.*, 1981).

To gain more insight in these structural changes and in particular the influence of electrolytes upon them, the density and heat capacity of Synperonic NPE 1800 solutions have been measured in the presence and absence of electrolytes.

In order to obtain accurate heat capacity values, very accurate density values are needed. The latter have been measured using a Sodev flow digital densimeter (model 03D) described by Picker *et al.* (1974). The density $\rho$ of a liquid solution contained in a stainless tube is related to the vibration period $\omega$ of the tube

$$\rho = \rho_o + \beta_v (\omega^2 - \omega_o^2) \qquad (3.14)$$

where $\rho_o$ and $\omega_o$ are the density and vibration period of a reference solvent respectively. By using standard solvents the value of the constant $\beta$ has been determined as 27.690 kg $m^{-3}s^{-2}$ at 298.15 K (Zegers, 1982).

The densimeter was thermostatted with a Sodev CT11 flow temperature regulator capable of keeping the temperature constant to 1 mK. The frequency of the tube was measured with a high resolution digital frequency meter (Philips PM 6611 universal counter 80 MHz), the output of which was fed to an interface (PM 6611 Digitec 12-5 A.K. V.U. Amsterdam), which in turn, was connected to a printer (Digitec 6410 S). All measurements were carried out at 298.15 K. The flow rate was less than $5 \cdot 10^{-9} m^3 s^{-1}$. Under these conditions differences in densities smaller than $2 \cdot 10^{-3}$ kg $m^{-3}$ and in most cases even smaller than $1 \cdot 10^{-3}$ kg $m^{-3}$ could be measured. The density of water at 298.15 K was taken from the literature $\rho_o$=997.047 kg $m^{-3}$ (Kell, 1967).

Differences in heat capacities per unit volume ($\sigma_c$) were measured using a Picker flow microcalorimeter (Systeme Picker, Setaram, Lyon, France). The principle of the instrument has been described in detail by Picker *et al.* (1971). Essentially, two liquids at the same temperature, $T_o$, which are flowing at the same rate in twin cells, are heated simultaneously, and the difference in the applied power ($\Delta W$), necessary to keep the final temperature of both liquids constant ($T_o+\Delta T$) is proportional to the difference in heat capacity per unit volume ($\Delta\sigma_c$) of the two liquids (Desnoyers *et al.*, 1976). If a fraction $f_c$ of the applied power serves to increase the temperature of the liquids in the flow cells, then:

$$\frac{\Delta W}{f_c W_o} = \frac{\Delta \sigma_c}{\sigma_{c,o}} \qquad (3.15)$$

where $W_o$ is the basic power applied to the cells and $\sigma_{c,o}$ the heat capacity per unit volume of the reference liquid. The value of $f_c$ is an apparatus constant and has been measured separately ($f_c$ = 0.9874, Zegers, 1982). The liquids were sucked through the calorimeter by means of a bent axis rotary pump of Picker design (Setaram, France) using a separator. This separator prevents the pump from direct contact with the liquid and also smoothes the pulses orginating from the pump. For a proper use of the instrument it is essential that the induced temperature change ($\Delta T$) is kept small and as constant as possible. This can be achieved by adjusting the flow rate. With a flow rate of $8 \cdot 10^{-9} m^3 s^{-1}$ and a heating

power $W_o$ of 20.5 mW, the induced temperature change was 0.6 K. The calorimeter was thermostatted with a Sodev CT-C flow temperature regulator (Picker *et al.*, 1968).

Each measurement was performed with the previous sample as reference, taking water as the first solution. After measuring the heat capacity of a new solution for the first time, the procedure was reversed, and in this second experiment the reference was measured relative to the sample. This means that a negative value of the difference in basic power $\Delta W^*$, necessary to maintain the final temperature of both liquids was recorded. This can be related to the differences in heat capacities per unit volume in the following way:

$$\frac{\Delta W^*}{f_c W_o + \Delta W^*} = \frac{-\Delta\sigma_c}{\sigma_{c,o}} \qquad (3.16)$$

Finally the heat capacity was measured for the third time, in the same setting as the first measurement. It appeared that under these conditions the overall precision is better than 100 J $K^{-1}m^{-3}$. The value of the heat capacity per unit volume of the reference solvent (in this case water) under the same conditions as the experiments were performed was taken from the literature $\sigma_w = 4.167 \cdot 10^6$ J $K^{-1}m^{-3}$ (Stimson, 1955).

### 3.4.2 Results and discussion

#### 3.4.2.1 *Apparent molal volumes in water*

From the experimental densities of aqueous Synperonic NPE solutions the apparent molal volumes $\phi_{v,s}$ of the surfactant have been calculated from the following equation (Musbally *et al.*, 1974; De Visser *et al.*, 1978):

$$\phi_{v,s} = \frac{M_s}{\rho} - \left(\frac{\rho - \rho_o}{m_s \rho \rho_o}\right) \qquad (3.17)$$

where $M_s$ and $m_s$ are the molecular mass and molality of the surfactant respectively and $\rho_o$ is the density of the solvent. The results are given in fig. 3.4 and in table 3.3 (see appendix).

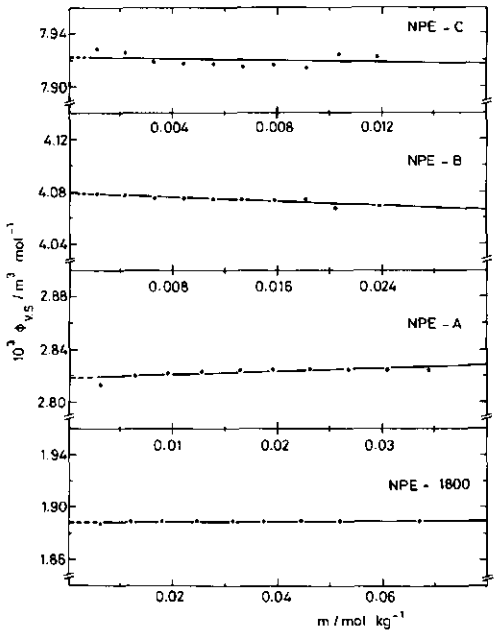


Fig. 3.4 Apparent molal volumes of various Synperonic NPE's in water at 298.15 K

For dilute solutions of non-polar solutes the results are usually expressed in an equation of the form (De Visser *et al.*, 1978):

$$\phi_{v,s} = \phi^{o}_{v,s} + A_{v,s} \cdot m \qquad (3.18)$$

where $\phi^{0}_{v,s}$ is the apparent molal volume at infinite dilution (a value which is equal to the standard partial molar volume $\bar{V}^{0}_{s}$) and where $A_{v,s}$ is the inital slope. Values of $\phi^{0}_{v,s}$ and $A_{v,s}$ obtained by a least squares fit of the results of different Synperonic NPE surfactants to equation 3.18 are presented in table 3.4.
Due to the low c.m.c.'s of these nonionic surfactants, no results could be obtained for the pre-micellar region (see section 3.3.2).

Table 3.4 Parameters of equation 3.18 of various Synperonic NPE in water at 298.15 K

| Surfactant | $\phi^0_{v,s}$ (= $\bar{V}^0_{s,m}$) ($dm^3 mol^{-1}$) | $A_{v,s}$ ($dm^3 mol^{-2} kg$) |
|---|---|---|
| NPE 1800 | 1.889 ± 0.001 | 0.02 ± 0.01 |
| NPE A | 2.818 ± 0.002 | 0.28 ± 0.09 |
| NPE B | 4.079 ± 0.001 | -0.42 ± 0.07 |
| NPE C | 7.923 ± 0.003 | -0.37 ± 0.48 |

Therefore $\phi^0_{v,s}$ is the standard partial molal volume *in the micellar state*. No physical meaning should be assigned to the parameter $A_{v,s}$.

From fig. 3.4 it can be seen that the measured apparent molal volumes are nearly independent of the surfactant concentration for all different NPE surfactants. Similar results have been found for ionic surfactants (Musbally *et al.*, 1974; Kale and Zana, 1977; Brun *et al.*, 1978; De Lisi *et al.*, 1980). Ionic surfactants which have a higher c.m.c. compared to nonionic surfactants, are usually measured over a broader concentration region. In the pre-micellar region the apparent molal volume does not change much, increases sharply at the c.m.c. and levels off slowly at higher concentrations to a nearly constant value.

For the Synperonic NPE-surfactants a linear relation is observed between $\bar{V}^0_s$ and the number of ethoxy groups (fig. 3.5). From the intercept of this graph the standard partial molal volume of the common core is found to be $(0.96 \pm 0.02) \cdot 10^{-3} m^3 mole^{-1}$. This value can be compared with the molar volumes, derived from density measurements found in the literature of the constituents of the nonylphenol polypropylene oxide core. The density of nonylphenol is 953 kg $m^{-3}$ (I.C.I., 1981) and that of a propylene oxide monomer is 1173 ± 32 kg $m^{-3}$ (an average of the values collected by Brandrup and Immergut, 1966). This gives a theoretical molar volume of

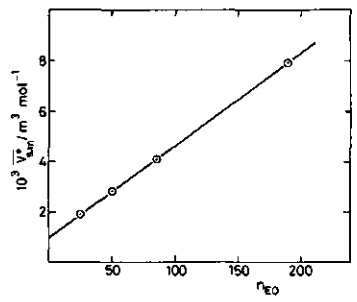


Fig. 3.5 Partial molal volumes for various Synperonic NPE's in water at 298.15 K

$0.91 \cdot 10^{-3} m^3 mole^{-1}$. The latter value agrees reasonably well with that determined from the molar volume, within experimental error. From the slope of fig. 3.5 a volume of $(36.7 \pm 0.2) \cdot 10^{-3} m^3 mole^{-1}$ can be derived for one ethylene oxide monomer. This is identical to the value obtained by Andersson (1963).

Finally it can be concluded that the density measurements are self consistent and support the findings that Synperonic NPE surfactants differ only in the amount of ethylene oxide groups.

### 3.4.2.2 *Influence of electrolytes on apparent molal volumes*

For binary mixtures (see previous section) the apparent molal quantity $\phi_v$ is generally measured as a function of concentration of one of the components, which can be calculated in a straightforward way. In the case of ternary mixtures the choice of a proper concentration scale for one component is not obvious. One possibility is to express all concentrations relative to the pure solvent (the so called MacMillan-Mayer approach) (De Visser *et al.*, 1977b). This approach is usually applied at low concentrations of the second dissolved component. Another possibility is to express the concentration as mean molality $\bar{m}$ (number of moles Synperonic NPE per kg of mixed solvent, De Visser et al., 1977b) or aquamolalities

(number of moles Synperonic NPE per 55.51 moles of mixed solvent, Musbally *et al.*, 1976). Due to the low concentrations of electrolytes relative to water it was found preferable to express all concentrations of surfactant relative to pure water.

Densities of the ternary system water-electrolyte-surfactant have been measured relative to the binary system water-electrolyte. Data for these binary systems are available in the literature (Millero, 1972). Data for $Na_2SO_4$ were taken from the polynomial of Perron *et al.* (1975) and for NaCl from Perron *et al.* (1981). Our procedure was occasionally checked by measuring some additional points of the binary electrolyte mixture. The values coincided exactly with the given polynomials. The apparent molal volume of the third component (Synperonic NPE 1800) can be calculated from the equation:

$$\phi'_{v,s} = \frac{M_s}{\rho'} - \frac{M_e x_e + M_{wa} x_{wa}}{x_s} \cdot \frac{\rho' - \rho'_o}{\rho' \rho'_o} \qquad (3.19)$$

where M and x are the molecular mass and mole fraction respectively; the subscripts s, e and wa referring to surfactant, electrolyte and water respectively; $\rho'_o$ is the density of the solution which is used as the reference (in this case the electrolyte-water mixture) and $\rho'$ is the density of the ternary system. The apparent molal property calculated with equation 3.19 is only "apparent" relative to the binary water-electrolyte system and not to pure water. Equation 3.19 is similar to the one given by Lara *et al.* (1981).

Results for two types of electrolytes at two different concentrations are given in table 3.5 (see Appendix) and in fig. 3.6. The apparent molal volume depends on the surfactant concentration. This is in contrast with the results obtained in the absence of electrolytes. A possible explanation could be that the transition from single-dispersed molecules to micelles is less sharp in the presence of electrolytes as suggested by Musbally *et al.* (1976). These latter authors found a similar effect for the apparent molal volumes of a cationic surfactant in water in the presence of urea.

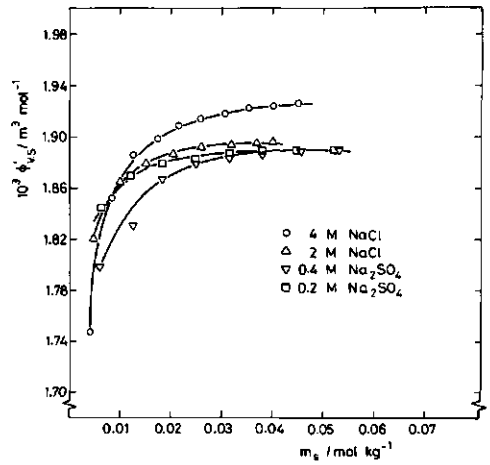


Fig. 3.6 Effect of electrolytes on the apparent molal volumes of Synperonic NPE 1800 at 298.15 K

According to these authors a better approach is to express the results as partial molal quantities. The change in volume from a monomeric surfactant to the volume of a surfactant in the micelle can be expressed by:

$$\Delta V_m = \bar{V}^o_{s,m} - \bar{V}^o_{s,s} \qquad (3.20)$$

Generally the value of $\Delta V_m$ is positive, because the standard partial molal volume of the hydrocarbon chain of the surfactant is lower than the molal volume of the same pure (liquid) part of the surfactant. Free alkyl chains seem to fit, at least partially, in the natural cavities of liquid water (Desnoyers *et al.*, 1980). The value of $\Delta V_m$ for the nonionic surfactants used in this study could not be determined, because of the lower concentration limit of the experimental technique. If $\phi'_{V,S}$ values are measured at fairly close spaced molalities, the partial molal volumes can be derived from a plot of $\Delta\,(\phi'_{V,S}.m)/\Delta m$ against the mean molality.

This is shown in fig. 3.7. From this graph it appears that the partial molal volumes beyond the c.m.c. are independent of the surfactant concentration in the presence of electrolytes. The values of $\bar{V}^{o}_{s,m}$, the standard partial molal volume in the micellar state, obtained by extrapolation are given in table 3.6. It is noted that the effect of 4 M NaCl is relatively larger than that of the other electrolyte concentrations.

Table 3.6 Partial molal volumes ($\bar{V}^{o}_{s,m}$) of Synperonic NPE 1800 in the presence of some electrolytes at 298.15K

| Solvent | $\bar{V}^{o}_{s,m}$ ($dm^3 mol^{-1}$) |
|---|---|
| water | 1.889 ± 0.001 |
| 0.2 M $Na_2SO_4$ | 1.897 ± 0.002 |
| 0.4 M $Na_2SO_4$ | 1.904 ± 0.003 |
| 2 M NaCl | 1.908 ± 0.003 |
| 4 M NaCl | 1.946 ± 0.008 |

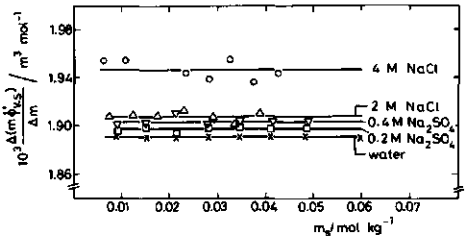


Fig. 3.7 Effect of electrolytes on the partial molal volumes of Synperonic NPE 1800 at 298.15 K

Høiland and Vikingstad (1978) studied the effect of NaCl on the partial molal volumes of sodium dodecanoate. They found an opposite trend: a slight decrease in $\bar{V}^{o}_{s,m}$ with increasing NaCl molality. The relatively high c.m.c. value of sodium dodecanoate enabled them to measure also $\bar{V}^{o}_{s,s}$ and they found an increase in this quantity with increasing NaCl molality. The obtained $\Delta V_m$ values decreased linearly with increasing concentration of added NaCl. They explained this decrease in $\Delta V_m$ by the increased association of sodium ions to the micelles as the concentration of NaCl increased. Measurements of the partial molal volumes of a homologous series of sodium alkyl carboxylates seem to support this explanation (Vikingstad *et al.*, 1978).

One would expect that the standard partial molal volume of a non-ionic surfactant in the monomeric state ($\bar{V}^{o}_{s,s}$) will change depending on the nature of added electrolyte. The presence of NaCl, which is slightly structure forming, will reduce the natural cavities of water, and therefore a small increase in $\bar{V}^{o}_{s,s}$ will be expected, assuming that there is no interaction between the surfactant and the ion itself. This small increase will be minor relative to the experimentally determined effect of NaCl on $\bar{V}^{o}_{s,m}$. The resulting increase in $\Delta V_m$ could possibly be explained by a partial salting-out phenomenon of the polypropylene oxide part and polyethylene oxide part of the Synperonic NPE surfactant.

### 3.4.2.3 *Heat capacities in water*

The apparent molal heat capacity ($\phi_{c,s}$) of the surfactant can be calculated using the following equation (Simard and Fortier, 1981):

$$\phi_{c,s} = M_s c_p + (c_p - c_{p,o})/m_s \qquad (3.21)$$

in which $M_s$ and $m_s$ have the same meaning as in section 3.4.2.1, $c_p$ and $c_{p,o}$ are the specific heat capacity of the solution and the solvent respectively. The difference in specific heat capacity can be derived from the measured difference in heat capacity per unit volume by the relation:

$$c_p - c_{p,o} = c_{p,o} \cdot \left\{ \frac{\sigma_c - \sigma_{c,o}}{\sigma_{c,o}} + 1 \right\} \frac{\rho_o}{\rho} - c_{p,o} \qquad (3.22)$$

where $(\sigma_c - \sigma_{c,o})/\sigma_{c,o}$ can be found from equations 3.15 and 3.16. The results for Synperonic NPE 1800 in water are collected in table 3.3 (see Appendix) and in fig. 3.8.

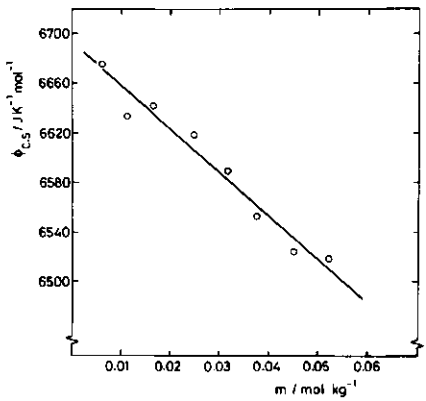


Fig. 3.8 Apparent molal heat capacities of Synperonic NPE 1800 in water at 298.15 K

The experimental error was found to be less than 0.5 %. The determination of $\phi_{c,s}$ at lower and higher molalities was impossible due to the concentration limits of the experimental technique. The calculated results were fitted by a least-squares method to an equation of the form:

$$\phi_{c,s} = \phi^o_{c,s} + A_{c,s} \cdot m \qquad (3.23)$$

where $\phi^o_{c,s}$ is the extrapolated value to infinite dilution, applying to micelles. The value of $\phi^o_{c,s}$ = 6694 J K$^{-1}$mol$^{-1}$ and is equal to the standard partial molal heat capacity ($\bar{c}^o_{p,sm}$). (De Visser *et al.*, 1977c). The value of the slope is $A_{c,s}$ = -3515 J K$^{-1}$mol$^{-2}$kg. Comparison with literature values for other nonionic surfactants is not possible since there are no reported values of $\bar{c}^o_{p,s}$ for

such surfactants. However, Desnoyers *et al.* (1980, with further references inthere) have undertaken systematic studies of the thermodynamic properties of some well-characterized ionic surfactants in water. They could measure these over a wide range of concentrations covering the pre- and post-micellar regions. The apparent molal heat capacities of ionic surfactants, found by these authors, showed a slow increase with concentration until the c.m.c. had been reached and then after the c.m.c. had been passed the apparent molal heat capacities showed a constant decrease. Sometimes around the c.m.c. a hump could be observed in such graphs. This can be qualitatively explained as follows. The very large value of the standard partial molal heat capacity of organic solutes in water is a characteristic of hydrophobic hydration (Desnoyers *et al.*, 1980). After the c.m.c. has been passed this hydrophobic hydration is reduced. Inside the micelle most of the hydrocarbon chains of the surfactants are no longer in contact with water and the standard partial molal heat capacity reaches approximately the value of an organic liquid. The results of the Synperonic NPE have been obtained after the c.m.c. and therefore are consistent with this qualitative picture. A constant value for the standard partial molal heat capacity could not be reached due to the concentration limit.

3.4.2.4 *Influence of electrolytes on heat capacities*

The heat capacities of the ternary water-electrolytes-surfactant system have been measured relative to a binary system in a similar way as the densities. The apparent molal heat capacity of the surfactant in such a ternary mixture has been calculated with the equation:

$$\phi'_{c,s} = M_s c'_p + \frac{M_e x_e + M_{wa} x_{wa}}{x_s} (c'_p - c'_{p,o}) \qquad (3.24)$$

in which $c'_p$ and $c'_{p,o}$ are the specific heat capacity of the ternary and binary system respectively. The other symbols are the same as those used in equation 3.19.

Results for two types of electrolytes at two different concentrations are given in table 3.5 (see Appendix) and fig. 3.9. No clear picture of the effect of addition of electrolytes emerges from this graph. A decrease in apparent molal heat capacity with increasing electrolyte concentration can be found at a concentration of 2 M NaCl. In the presence of 4 M NaCl and 0.2 M $Na_2SO_4$ the apparent molal heat capacity is nearly independent of the surfactant concentration. However an increase in the apparent molal heat capacity is found at a concentration of 0.4 M $Na_2SO_4$. A reduction in heat capacity should be expected due to a reduction of the hydrophobic hydration of the hydrocarbon chain similar to the heat capacity in the absence of electrolytes. However a limiting value for the apparent molal heat capacity seems to be reached, as has been predicted by Desnoyers *et al.* (1980), but which could not be measured in the absence of electrolytes. The observed reductions in heat capacity for 0.2 M $Na_2SO_4$ and the NaCl concentrations are consistent with the increase in partial molal volumes and with the qualitative picture of hydrophobic hydration. No good explanation can yet be offered for the increase of heat capacity in the case of 0.4 M $Na_2SO_4$.

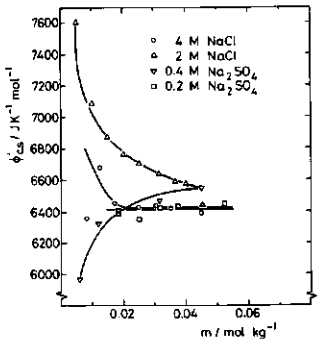


Fig. 3.9 Effect of electrolytes on the apparent molal heat capacities of Synperonic NPE 1800 at 298.15 K.

## 3.5 Light scattering

The excess light scattering of a surfactant solution gives valuable information on the weight average micellar molecular masses (and therefore some information about the size of the micelle) and about the shape. The basics of light scattering were formulated a considerable time ago by Rayleigh, Mie, Gans and Debye. For a review on light scattering one is referred to Stacey (1956), Tanford (1961) or to Huglin (1978).

The turbidities of surfactant solutions were measured using a Sofica Photo Gonio Diffusometer (model 42.000) at 298.1 K (see Baker *et al.*, 1984). The used wavelength was 436 nm. All solutions were passed twice through 0.2 μm Millipore membrane filters, the second time directly into the measuring cells. These cells were previously cleaned with chromic acid, distilled water and finally steamed with acetone vapor. The filtration unit was placed in a pressure cabinet to eliminate dust.

The micellar molecular mass (M) was determined by measuring scattering intensities at an angle of 90° as a function of the surfactant concentration and by using the Debye relation (Debye, 1947, 1949):

$$H \frac{(c - c_o)}{\tau - \tau_o} = \frac{1}{M} + 2B_2 (c - c_o) \qquad (3.25)$$

where H is a constant, c is the total concentration of surfactant, $\tau$ is the turbidity, $\tau_o$ the turbidity at $c_o$, and $B_2$ is the second virial coefficient which describes the extent of interaction between the scattering particles. Unassociated surfactant contributes to a negligible extent to the total turbidity of micellar solution at or above the c.m.c. Therefore $\tau_o$ was taken equal to the turbidity of solvent.

The constant H is given by:

$$H = \frac{32\pi^3 n_s^2 (dn/dc)^2}{3N_{Av}\lambda^4} \qquad (3.26)$$

where $n_s$ is the refractive index of the solvent, $N_{Av}$ is Avogadro number, $\lambda$ is the wavelength in vacuo used and (dn/dc) is the re-

fractive index increment. This last quantity has been experimentally determined with a High accuracy Abbe 60 Refractometer at 298.1 K.

The scattered intensity was measured at angles of 60°, 90° and 120°. The ratio of the light scattered at 60° to that scattered at 120° is called the dissymetry. If this quantity is unequal to unity, this could be an indication of micellar nonspherity.

The scattered intensity at an angle of 90° is proportional to the turbidity:

$$\tau = k_L i_{90} \tag{3.27}$$

where $k_L$ is an instrument constant, which has to be determined using standards. As primary standard pure benzene has been used, from which the absolute turbidity at the wavelength of 436 nm and at 298.1 K is known from literature (Carr and Zimm, 1950; Huglin, 1978). Since the frequent use of benzene is undesirable (being carcinogenic) it is convenient to use a secondary standard of known turbidity relative to that of the primary standard. A solid cylindrical rod of perspex has been used for this purpose after this has been calibrated against pure benzene.

The scattered intensities had to be corrected for depolarization following the method of Cabannes (Huglin, 1978). For unpolarized incident light at an angle of 90° the Cabannes factor $f_c^u$ is given by:

$$f_c^u = \frac{6 + 6\rho_u}{6 - 7\rho_u} \tag{3.28}$$

where $\rho_u$ is the ratio between the horizontally and the vertically polarized components of the unpolarized incident beam (also known as the depolarization ratio). Equation 3.27 must be corrected by dividing by the Cabannes factor.

The trends found with light scattering are in accordance with expectations for ethoxylated nonionic surfactants (see fig. 3.10 and table 3.7). Surfactants with a long ethoxy chain lenght form micelles with a small number of molecules. Conversely surfactants with a short ethoxy chain length form micelles with a large number

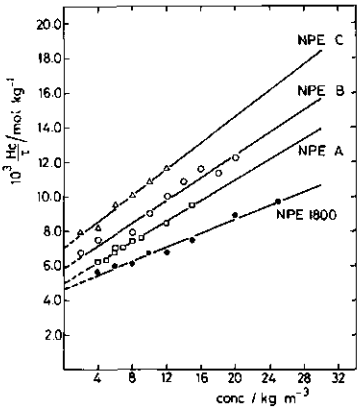


Fig. 3.10 Debye plots for Synperonic NPE surfactants in water at 298.1 K

Table 3.7 Light scattering data for Synperonic NPE surfactants in water and for Synperonic NPE 1800 in different solvents at 298.1 K

| Surfactant | Solvent | M (kg mol$^{-1}$) | $B_2$ (mol m$^3$kg$^{-2}$·10$^{-4}$) | m |
|---|---|---|---|---|
| NPE 1800 | water | 214.2 ± 7.7 | 0.99 ± 0.06 | 102 ± 15 |
| NPE A | water | 201.1 ± 3.3 | 1.50 ± 0.09 | 63 ± 4 |
| NPE B | water | 173.3 ± 10.2 | 1.64 ± 0.14 | 37 ± 3 |
| NPE C | water | 142.9 ± 4.3 | 1.91 ± 0.14 | 15 ± 1 |
| NPE 1800 | 0.4 M $Na_2SO_4$ | 207.4 ± 3.0 | 0.26 ± 0.04 | 99 ± 14 |
| NPE 1800 | 4 M NaCl | 520 ± 180 | -0.4 ± 0.5 | 250 ± 90 |

of molecules (El Eini *et al.*, 1976). The second virial coefficient increases with the polyoxyethylene chain length of the NPE molecule, reflecting the increasing aqueous solubility of the monomer. This is consistent with the decrease in the micellar molecular weight with the increase in the polyoxyethylene chain length. Becher (1961)

gave an empirical relation between the aggregation number m and the number of ethylene oxide units $n_{EO}$ for polyoxyethylene derivatives:

$$m = a_B/n_{EO} + b_B \qquad (3.29)$$

where $a_B$ and $b_B$ are constants. This equation predicts an infinitely large micelle, when there are no ethoxy groups present, i.e. complete insolubility of the core compound. No association occurs when m is equal to unity. Our results also showed a linear relation as predicted from equation 3.29 (see fig. 3.11). Since the intercept is significantly larger than 1, the results also indicate that there always occurs association above a certain concentration for each surfactant of the Synperonic NPE series independently of the number of ethoxy groups. The dissymetry of the Synperonic NPE surfactants shows no deviation from unity, but this does not definitely exclude the possibility that the micelles are asymmetrical.

The effect of electrolyte is clearly demonstrated in fig. 3.12. In the case of 0.4 M $Na_2SO_4$ the weight average micellar molecular mass is nearly the same as in the absence of electrolyte, but the second virial coefficient is smaller, indicating that the extent of interactions between the scattering particles is weaker.

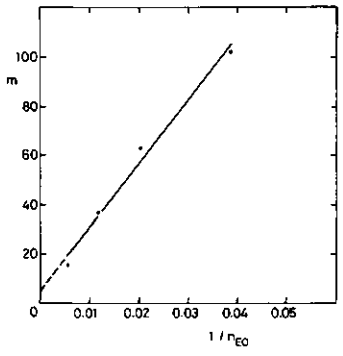


Fig. 3.11 Aggregation number m as a function of the reciprocal average ethylene oxide units following Becher (1961).

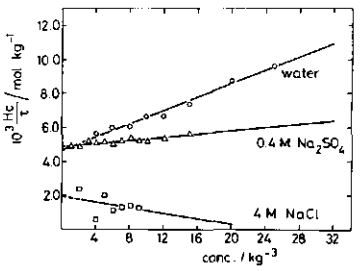


Fig. 3.12 Debye plots for Synperonic NPE 1800 in different solvents at 298.1 K

In the presence of 4 M NaCl a negative second virial coefficient is found indicating a salting-out phenomenon. This is supported by a relatively large micellar molecular weight (2.5 times larger than in absence of electrolyte) and by a large dissymmetry ratio (1.3).

## 3.6 Viscosities

As mentioned before the viscosity of a micellar solution is very sensitive to the size and shape of the micelles. The theories of viscosity have only been developed for the ideal cases of non-interacting particles in dilute solutions. Application of these theories to micellar solutions is not straightforward since the interaction between the micelles must be taken into account (Wennerström and Lindman, 1979).

In order to gain more information on the surfactants used in this study, their viscosities have been determined using an Ubbelohde suspended level dilution viscosimeter. The reduced viscosities $[\eta(\text{solution}) - \eta(\text{solvent})]/[\eta(\text{solvent})\cdot(c - \text{c.m.c.})]$ are plotted as a function of the micellar concentration to obtain the intrinsic viscosity $[\eta]$ by extrapolation to zero concentration. The density differences between the micellar solution and the solvent have been neglected and the assumption was made that the viscosity of the solvent is equal to the viscosity of the monomer surfactant solution at or above the c.m.c.

The linear dependence of the reduced viscosities on the surfactant concentration can be represented by a Huggins-type equation (Van den Boomgaard *et al.*, 1983):

$$\frac{\eta_{sp}}{c - c.m.c} = [\eta] + [\eta]^2 \cdot k_H \, (c - c.m.c) \qquad (3.30)$$

where $k_H$ (the Huggins constant) is a measure of the interaction between the micelles and the intrinsic viscosity is a measure of the size of the micelle. The application of equation 3.30 to obtain $[\eta]$ must be considered with some reservation, since the average size of the micelle is not constant, probably increasing with c and hence $[\eta]$ is dependent on c (Nagarajan *et al.*, 1982). Therefore $k_H$ is not a pure interaction energy parameter but it also contains a size factor. Moreover $k_H$ is sensitive to the shape of the micelle which affects the hydrodynamic interaction between pairs of particles (Tanford *et al.*, 1977). Without independent information on micellar size and shape these different contributions to $k_H$ can not be unraveled. If the micelles are cylindrical, the rigidity of the particles may pose another problem (see e.g. Bohdanecký and Kovár, 1982) although Nagarajan (1982), on the basis of model analyses of various types of surfactants concluded that rigidity prevails. Irrespective of these complications, it appears that the slope and intercept are suitable measures of the solvent quality.

In literature many different values of $k_H$ have been reported. Bohdanecký and Kovár listed various values between 0.40 and 2.26 for rigid non-interpenetrating spheres, with the probably best value being 0.69 (Peterson and Fixman, 1963). The divergence between the various experiments illustrates the great difficulty in describing the hydrodynamics of interaction.

Reduced viscosities as a function of the surfactant concentration for Synperonic NPE with different ethoxy chain lengths at 298 K are plotted in fig. 3.13a. The intrinsic viscosity increases with the chain length reflecting the increase in size of the micelle. The Huggins coefficient has a maximum value for NPE B.

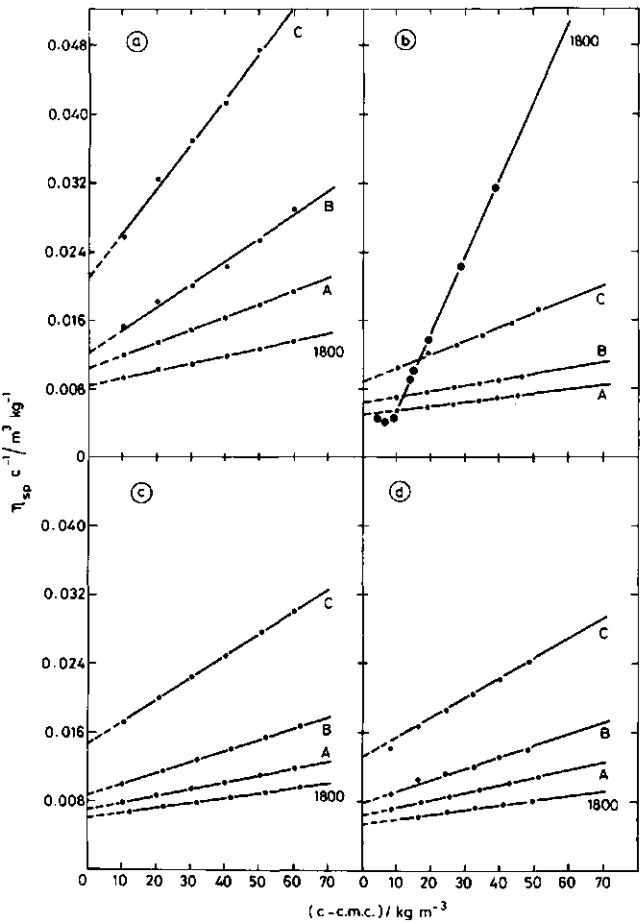


Fig. 3.13 Reduced viscosities of various NPE surfactants at 298 K

a) no eletrolyte added b) 4 M NaCl

c) 0.4 M $Na_2SO_4$ d) 4 M NaBr

Deviation of the $k_H$ value from the theoretical value for rigid non-interpenetrating spheres has often been ascribed to nonspherity (Schott, 1967; El Eini et al., 1976). However it is not very realistic to consider the Huggins coefficient as an accurate measure of the shape of a micelle. Firstly, as indicated above, many different values for $k_H$ have been proposed, even for rigid spheres. Most articles concerning micellar dimensions quoted a value of $k_H = 2.00$ given by Tanford (1961), which is obviously not the correct value for rigid spheres. Secondly, the comparison between micelles composed of surfactants with different ethoxy chain lengths is probably not straightforward since these surfactants are likely to deform in different ways under shear flow. Thirdly, it is known that for polymer coils the Huggins coefficient is concentration dependent (Yamakawa, 1972). This will influence the shape of micelles composed of surfactants with different ethoxy chain length due to difference in segment concentration. Therefore it seems to be more realistic to treat the Huggins coefficient only as a qualitative measure of the solvent quality. This is illustrated in fig. 3.14 in which the reduced viscosities for NPE 1800 are plotted for different temperatures.

Table 3.8 summarizes the pertaining parameters. As can be seen from this table the Huggins coefficient increases with decreasing temperature, indicating that the hydrodynamic interaction increases with decreasing temperature. This interaction is not likely to be determined by the shape of the particles since the reverse trend would be expected. The surfactants become less soluble with increasing temperature, and therefore tend to make bigger, i.e. more elongated micelles at higher temperature. Hence, the observed trend must apparently be attributed to the decreasing solvation with increasing temperature in such a way that the reduction in effective size, as expressed through the coefficient $[\eta]^2$, is not enough to account for the whole effect.

This interpretation is also partly in line with the results for the Synperonics of higher ethoxy chain length. For NPE A and B we found the Huggins coefficient to exceed the value for NPE 1800, but for NPE C we found a lower value. The latter result can probably be attributed to the more polymeric character of this sur-

Table 3.8 Parameters of equation 3.30 for Synperonic NPE 1800 at various temperatures.

| Temperature (K) | | 278 | 285 | 291 | 298 | 310 | 323 |
|---|---|---|---|---|---|---|---|
| $[\eta]$ | $(m^3 kg \cdot 10^{-3})$ | 8.6 | 8.4 | 8.2 | 8.1 | 7.5 | 6.5 |
| $k_H$ | (-) | 2.0 | 1.4 | 1.2 | 1.0 | 1.0 | 0.9 |

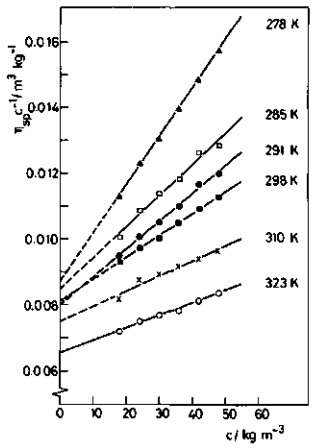


Fig. 3.14 Reduced viscosities of NPE 1800 solutions at various temperatures. No electrolytes added.

factant, which could lead to a bigger deformation of the total micelle in shear flow.

The reduction of intrinsic viscosity with increase of temperature can probably be attributed to a reduction in hydration of the EO-mantle of the micelle; this will be treated in the following section. Addition of electrolytes also reduces the intrinsic viscosity with no clear ion-specifity as can be seen from fig. 3.13 b-d. This decrease is due to the decreased solvency. The trend of

the variation of the Huggins coefficient as a function of the ethoxy chain length is similar to that in water. Again a maximum value for $k_H$ is obtained for NPE B. For Synperonic NPE 1800 the Huggins coefficient as a function of ion strength passes through a maximum (fig. 3.15). This indicates that there are two counteracting effects on the hydrodynamic interaction. More information about the effect of the electrolytes on the size and shape is needed for further analysis of these two opposing trends. Ion incorporation into the micelle must also be considered, and this could also explain the peculiar results of NPE 1800 in 4 M NaCl compared with NPE 1800 in more dilute (1 M) NaCl and in other electrolytes at any concentration studied. This may be related to ion incorporation into the micelle, probably into the PPO part. By virtue of the higher polarizability of the anion, it must be expected that this incorporation is primarily determined by the anion, so that the specific effect of concentrated NaCl is a specificity of the $Cl^-$ ion over the $SO_4^=$ ion. This is also illustrated in fig. 3.13b where a dramatic difference between NPE 1800 and the other three can be found. It looks as if extension of the EO-part 'screens' the binding of $Cl^-$ ions to the PPO moiety. In contrast to this, 4 M NaBr behaves quite 'normal' (fig. 3.13d).

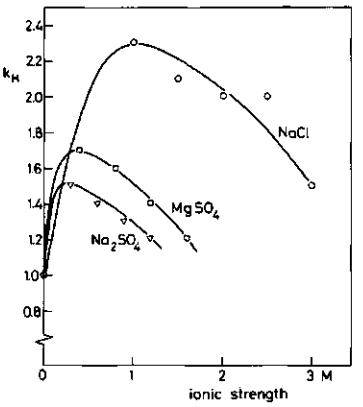


Fig. 3.15 Dependence of the Huggins coefficient $k_H$ of NPE 1800 micelles on the nature and concentration of the electrolyte at 298 K

The exact reason for this difference is difficult to establish; for one thing one would expect $Br^-$ ions to be incorporated in the micelles more easily than $Cl^-$ ions because of their higher polarizability but this is contrary to the results obtained. Whatever the reason may be, it is clear that viscometry is a sensitive tool to observe such differences.

## 3.7 Viscosities of poly(ethylene oxide) solutions

As has been pointed out in the previous sections of this chapter, the solvent quality plays an important role in the solution behaviour of NPE-surfactants. As the solution properties of these surfactants are to a large extent determined by poly(ethylene oxide), it is worthwhile to study the solution properties of this polymer separately. The solvent quality determines to a large extent polymer conformation in solution. This quality can be conveniently assessed by viscosimetry. Therefore a study was undertaken of the viscosity of PEO in water, and in some electrolyte solutions.
For some relevant literature one is referred to Kurata and Stockmayer (1963), Yamakawa (1971) and Bohdanecký (1982).

### 3.7.1 Experimental

All PEO samples used in this study are of commercial grade. PEO 20,000 and 35,000 have been obtained from Hoechst, PEO 100,000 and 200,000 from Aldrich and PEO 300,000 and 600,000 from B.D.H. They have been used without further purification.

All solutions were prepared by weight. The polymer concentrations were expressed as weight of polymer per weight of water. The solutions were filtered through a Millipore membrane filter (pore size $0.25 \cdot 10^{-6}$ m) under nitrogen pressure. To avoid any dust all work with these solutions was done in an anti-dust cabinet (Slee).

Viscosity measurements were performed with an automatic viscosimeter (Viscomatic MS type 53,000; Fica, France) with a photo-electric elution time determination and an automatic dilution module. The Ubbelohde capillary was cleaned with diluted chromic acid, after which it was rinsed with filtered deionised water and finally with solvent. The temperature was controlled within 0.005 K. The

elution time for water was 275 s at 298.15 K. Each series consisted of six different polymer concentrations. Density differences due to the added polymer and shear corrections were neglected. The overall inaccuracy of the measurements was less than 0.5%.

### 3.7.2 Theoretical aspects

The intrinsic viscosities were calculated according to the Huggins equation:

$$\eta_{sp}/c = [\eta] + [\eta]^2 \cdot k_H \cdot c \qquad (3.31)$$

The intrinsic viscosity of a polymer solution is related to the molecular mass by the well-known Mark-Houwink-Sakurada (MHS) equation:

$$[\eta] = K \cdot M^a \qquad (3.32)$$

where K and a are empirical parameters depending on the polymer and on the polymer-solvent interaction. A series of monodisperse polymer homologues should be used to obtain the appropriate values of K and a. For polydisperse samples M must be replaced by the viscometric average molecular mass $M_v$.

*Under theta-conditions, where the deviation from the random flight* conformation caused by attractive forces between chain units is exactly counterbalanced by the excluded volume effect, the value of a is 0.5. The corresponding $K_o$-value will reflect these short attractive forces and is therefore a polymer constant, which is defined as:

$$K_o = \phi_o \left(\frac{\langle h_o^2 \rangle}{M}\right)^{3/2} \qquad (3.33)$$

where $\phi_o$ is a universal constant with the theoretical value of $2.872 \cdot 10^{23} mol^{-1}$ and $\langle h_o^2 \rangle$ is the unperturbed mean square end-to-end distance. This $\langle h_o^2 \rangle$ can be calculated from random flight statistics (Flory, 1953; Tanford, 1961) and it is a function of the *number of chain units, the length of each unit, the angle between* two successive chain units and the restriction in rotation.

Another molecular dimension which can be used to describe the conformation of a polymer is the unperturbed mean square radius of gyration $\langle s_o^2 \rangle$. It can be shown that:

$$\langle h_o^2 \rangle = 6 \langle s_o^2 \rangle \tag{3.34}$$

All the above equations apply to theta conditions. In a better solvent the polymer coil will expand due to self-exclusion. Therefore, corrections have to be applied for the perturbed coil dimensions by introducing expansion factors which increase with increasing solvent quality.

$$\langle h^2 \rangle = \alpha_h^2 \langle h_o^2 \rangle \tag{3.35a}$$

$$\langle s^2 \rangle = \alpha_s^2 \langle s_o^2 \rangle \tag{3.35b}$$

An expansion factor $\alpha_\eta$ can also be obtained for the hydrodynamically effective coil radius from viscosity. However, $\alpha_\eta$ is unequal to $\alpha_h$ or $\alpha_s$ because the conditions of the non-free draining coils are no longer fullfilled. The viscometric expansion factor is defined as (Yamakawa, 1971):

$$\alpha_\eta^3 = [\eta]/[\eta]_\theta \tag{3.36}$$

These expansion factors can be expressed as functions of the excluded volume parameter z, a dimensionless quantity which is given by:

$$z = (4/\sqrt{27})\, C_M\, (\tfrac{1}{2}-\chi)\, M^{\frac{1}{2}} \tag{3.37}$$

with:

$$C_M = \left(\frac{27}{(32\pi)^{3/2}}\right) \left(\frac{\bar{V}_p^2}{V_1 N_{Av}}\right) \left(\frac{M}{\langle h_o \rangle}\right)^{3/2} \tag{3.38}$$

where $\bar{V}_p$ is the partial specific volume of the polymer, $V_1$ is the molar volume of the solvent and $\chi$ is the well-known Flory-Huggins polymer-solvent interaction parameter. The factor $\chi$ is a quantitive measure for the solvent quality and will, therefore, be an important parameter in this study. The expansion factors $\alpha_h$ and $\alpha_s$ can both be written as power series in z:

$$\alpha_h^2 = 1 + 1.333\, z - \ldots \tag{3.39a}$$

$$\alpha_s^2 = 1 + 1.276\, z - \ldots \tag{3.39b}$$

Table 3.9 Viscosity average molecular masses, intrinsic viscosities and Huggins coefficients of commercial PEO samples in water and some electrolyte solutions at 298.15 K

| Solvent | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | $Na_2SO_4$ | | | | | | | | |
| Sample | $M_v$ | 0 | | 0.1 | | 0.2 | | 0.3 | | 0.4 | | | | | |
| | $(kgmol^{-1})$ | $[\eta]$ $(kgkg^{-1})$ | $k_H$ (-) | $[\eta]$ $(kgkg^{-1})$ | $k_H$ (-) | $[\eta]$ $(kgkg^{-1})$ | $k_H$ (-) | $[\eta]$ $(kgkg^{-1})$ | $k_H$ (-) | $[\eta]$ $(kgkg^{-1})$ | $k_H$ (-) | | | | |
| H 20.000 | 19.4 | 36.18 | 0.3152 | 33.06 | 0.3070 | 30.76 | 0.3126 | 28.44 | 0.2829 | 26.42 | 0.3441 | | | | |
| H 35.000 | 33.5 | 54.44 | 0.2917 | 49.68 | 0.3337 | 44.62 | 0.3022 | 39.15 | 0.3994 | 36.29 | 0.3400 | | | | |
| A 100.000 | 84.4 | 108.95 | 0.1498 | 97.31 | 0.1831 | 86.11 | 0.2609 | 75.69 | 0.2203 | 62.02 | 0.2542 | | | | |
| B 200.000 | 137.6 | 157.14 | 0.2448 | 141.05 | 0.2604 | 122.81 | 0.1762 | 109.08 | 0.1548 | 84.56 | 0.2248 | | | | |
| B 300.000 | 318.0 | 294.60 | 0.2255 | 274.71 | 0.2360 | 255.86 | 0.2804 | 196.31 | 0.2885 | 149.60 | 0.2402 | | | | |
| B 600.000 | 436.0 | 372.90 | 0.1966 | 333.24 | 0.2526 | 285.94 | 0.2653 | 226.88 | 0.2145 | 181.16 | 0.2599 | | | | |
| Solvent | | | | | | | NaCl | | | | | | | | |
| Sample | | 0 | | 1 | | 2 | | 3 | | 4 | | | | | |
| H 20.000 | 19.4 | 36.18 | 0.3152 | 31.27 | 0.3103 | 27.64 | 0.3981 | 23.66 | 0.3928 | 19.89 | 0.3701 | | | | |
| H 35.000 | 33.5 | 54.44 | 0.2917 | 46.68 | 0.3218 | 39.69 | 0.3708 | 33.25 | 0.3177 | 30.28 | 0.3059 | | | | |
| A 100.000 | 84.4 | 108.95 | 0.1498 | 92.81 | 0.2764 | 76.66 | 0.2981 | 63.35 | 0.1826 | 45.95 | 0.3437 | | | | |
| A 200.000 | 137.6 | 157.14 | 0.2448 | 133.18 | 0.2741 | 113.03 | 0.1961 | 90.92 | 0.1676 | 63.17 | 0.4380 | | | | |
| B 300.000 | 318.0 | 294.60 | 0.2255 | 257.60 | 0.2379 | 211.97 | 0.2147 | 169.19 | 0.1758 | 122.77 | 0.1359 | | | | |
| B 600.000 | 436.0 | 372.90 | 0.1966 | 319.96 | 0.2693 | 260.81 | 0.2182 | 207.58 | 0.2310 | 139.76 | 0.2334 | | | | |

Equations 3.39a and b are only valid in the close vicinity of theta conditions. A theoretical description does not exist yet for the hydrodynamic expansion factor of the dependance of $\alpha_\eta$ on z. Following Yamakawa (1971, p. 384) this factor can be expressed in a semi-empirical relation:

$$\alpha_\eta^3 = C_o + C_1 z \qquad (3.40)$$

with $C_o = 1$ and $C_1 = 1.05$ for $\alpha_\eta^3 < 1.6$ and $C_o = 1.05$ and $C_1 = 0.87$ for $0 < \alpha_\eta^3 < 2.5$. The combination of equations (3.32), (3.33), (3.36) and (3.40) results in the Stockmayer-Fixman-Burchard (SFB) equation:

$$[\eta] = K_o M_v^{\frac{1}{2}} (C_o + C_1 z) \qquad (3.41)$$

According to equation 3.41 a plot of $[\eta]M_v^{-\frac{1}{2}}$ versus $M_v^{\frac{1}{2}}$ should give a straight line and the value of $\chi$ can be calculated from the slope by means of equations (3.37) and (3.38).

### 3.7.3 Results and discussion

A number of values of the parameters of the MHS equation for PEO in water at 298.15 K can be found in literature e.g. Boucher and Hines (1978). However the latter values obtained have been determined with relatively low molecular mass samples compared to the samples used in the present study. These values, used to calculate molecular masses from the obtained viscosimetric data, tend to underestimate the molecular mass (Cohen Stuart *et al.*, 1982a). The same is true for the MHS-parameters obtained by Amu (1982) because these have been based on number average molecular masses. However, Molyneux (1975) has reviewed the viscosity data for PEO in water over a broad temperature range and has given a consistent pair of values at 298.15 K. Therefore it was preferred to adopt these K and a values:

$$[\eta] = 2.2 \cdot 10^{-5} M_v^{0.75} \qquad (3.32a)$$

Using equation (3.32a) the viscosity averaged molecular masses have been calculated for the different PEO samples. The results are summarized in table 3.9 together with the intrinsic viscosi-

ties and the Huggins coefficients measured in different electrolyte concentrations. With the obtained viscosity-averaged molecular masses in water, the MHS-parameters for the different electrolyte solutions have been established and are given in table 3.10.

Table 3.10 MHS-parameters for PEO in water and some electrolyte solutions at 298.15 K

| Solvent<br>- | K<br>($m^3 kg^{-1} \cdot 10^{-6}$) | a<br>- |
|---|---|---|
| water | 0.220 | 0.75 |
| 0.1 M $Na_2SO_4$ | 0.203 | 0.75 |
| 0.2 M $Na_2SO_4$ | 0.255 | 0.72 |
| 0.3 M $Na_2SO_4$ | 0.321 | 0.69 |
| 0.4 M $Na_2SO_4$ | 0.558 | 0.62 |
| 1 M NaCl | 0.187 | 0.75 |
| 2 M NaCl | 0.201 | 0.73 |
| 3 M NaCl | 0.215 | 0.71 |
| 4 M NaCl | 0.419 | 0.62 |

These results show a decrease of a with increasing electrolyte concentration for both types of electrolytes as expected.

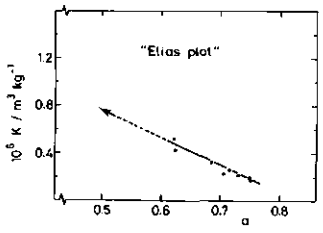


Fig. 3.16 MHS-parameters K and a for PEO in aqueous solutions at 298.15 K

According to Molyneux (1975) it has been empirically shown by Elias that a linear relation between K and a exists for a given polymer in different solvents. The same also applies to our data, as is shown in fig. 3.16. Under theta conditions (a = 0.5) this plot yields a value $K_o = 0.755 \cdot 10^{-6}$ $m^3 kg^{-1}$. This value should be considered with some reservation, because of the empirical character of the plot and the long extrapolation.

Using intrinsic viscosities and the molecular masses obtained with the MHS-equation, SFB-plots of PEO in water and in different electrolyte concentrations were constructed and are shown in fig. 3.17a and b. Since equation 3.41 is only valid at small expansion factors, the SFB-plots have been calculated for the four low molecular weights only (Yamakawa, 1971; Koopal, 1981). $K_o$ values have been calculated from the intercepts and these are given in table 3.11. In order to calculate $\chi$ a value for $\phi_o$ had to be chosen. Flory (1969) gave as a reasonable value $\phi_o = 2.6 \cdot 10^{23}$ which was used. The calculated $\chi$-values are also given in table 3.11. For $\bar{V}_p$ the value of $0.833.10^{-3}$ $m^3 kg^{-1}$ (section 3.4) was used.

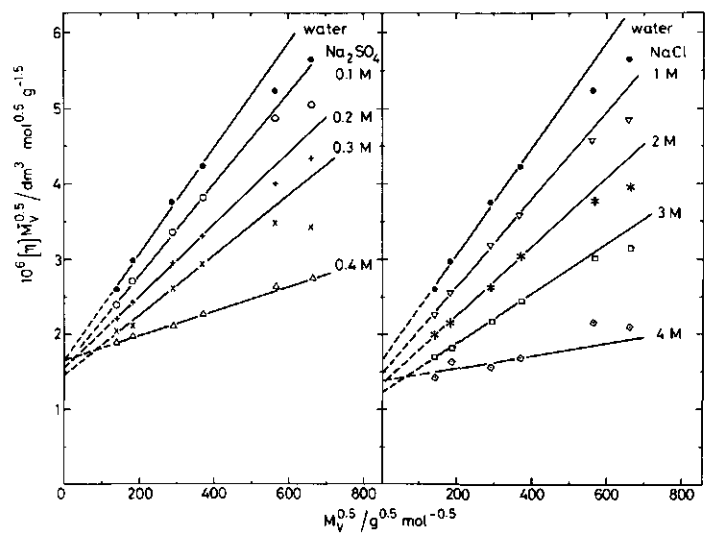


Fig. 3.17 Stockmayer-Fixman-Burchard plot for PEO in $Na_2SO_4$ solutions (a) and in NaCl solutions (b) at 298.15 K

In principle the electrolyte solutions should be treated as mixed solvents (Dondons and Patterson, 1969). As there is no appropriate information available on the solvent quality as a function of the mole fraction in the mixed solvent medium, the average molar volume $V_1$ of the solvent was used. This seems to be justified because even in the case of 4 M NaCl the mole fraction of the electrolyte is less than 0.02.

Table 3.11 SFB-parameters for PEO in water and some electrolyte solutions at 298.15 K

| Solvent | $K$ $(m^3 kg^{-1} \cdot 10^{-6})$ | $\chi$ (-) |
|---|---|---|
| water | 1.58 ± 0.07 | 0.426 |
| 0.1 M $Na_2SO_4$ | 1.49 ± 0.06 | 0.436 |
| 0.2 M $Na_2SO_4$ | 1.48 ± 0.03 | 0.450 |
| 0.3 M $Na_2SO_4$ | 1.38 ± 0.05 | 0.458 |
| 0.4 M $Na_2SO_4$ | 1.68 ± 0.02 | 0.486 |
| 1 M NaCl | 1.40 ± 0.06 | 0.439 |
| 2 M NaCl | 1.27 ± 0.03 | 0.452 |
| 3 M NaCl | 1.17 ± 0.02 | 0.465 |
| 4 M NaCl | 1.39 ± 0.15 | 0.493 |

Although the commercial polymer samples used in this study are certainly polydisperse, this was not taken into account in the above discussion. However, Koopal (1981) has demonstrated that the polydispersity corrections are constants when polymers with similar molecular masses distributions are used. For PEO the most common procedure of synthesis is condensation, which will lead to a Poisson distribution (chapter 2). This distribution is assumed to apply to all polymer samples used by us. According to Koopal (1978) this polydispersity will lead to relatively small errors in the slope of the SFB-plots in very good solvents and to no errors at all in nearly theta conditions.
Therefore no attempt has been made to calculate these errors.

As can be judged from the $\chi$-values (table 3.11) the solvent becomes worse upon addition of electrolytes. Although the absolute

values of the $\chi$-parameter may be affected substantially by the numerical constants used, which are somewhat uncertain, the relative values follow the same trend obtained from the results of the NPE-surfactants described in previous sections.

## 3.8 General discussion

For ionic surfactants it is often found that at high surfactant concentrations and/or high electrolyte concentrations the micelles grow in size. However it is still difficult to determine experimentally the shape of these aggregates in an unambiguous way. The question of whether non-spherical micelles are discs or rods, is still subject to a great deal of controversy. Tanford (1974, 1977) concluded from viscosity data that micelles, from ionic as well as nonionic surfactants, must have a disclike shape, which agreed well with his theoretical prediction. On the other hand it has been shown, in a convincing way, from light scattering (Mazer *et al.*, 1977) and viscosity measurements (Stigter, 1967) that when large micelles are formed, they are rod shaped. More detailed model calculations by Israelachvili *et al.* (1976) predicted micelle shapes with more complex boundaries than those of ellipsoids of revolution. An experimental test of their proposed model is difficult, because fluctuations in shape would have to be taken into account.

From thermodynamic considerations it can be derived that micellar solutions show a size distribution (Mukerjee, 1972). An indication of the width of such a distribution can be determined experimentally by measuring the ratio of different average micellar molecular masses. For instance, deviation from unity of $M_w/M_n$ is a measure for this width. An additional complication occurs in micellar systems, because the distribution of molecular masses is not simply unimodal but rather bimodal, possessing one peak at $Z_1$ corresponding to the monomer of the surfactant, and a second, distant peak at $Z_m$, corresponding to the micelles (Aniansson and Wall, 1974). Furthermore, the ratio between the heights of these modes is a function of the concentration. Becher (1965) showed that this will lead to different results for the number average and weight average of the micellar molecular masses. Therefore

an apparent width in the distribution will be found even for homodisperse surfactants. Attwood *et al.* (1970) measured this width experimentally both for a homodisperse ionic and a homodisperse nonionic micellar solution. They found within an error of 10 percent a value of unity for the ratio of the number average and weight average micellar molecular mass. This means that the effect of the bimodal distribution described by Becher should be less than 10 percent.

Heterodispersity of the surfactants has some impact on the composition, spatial structure and size distribution of the micelles. On the other hand Warr *et al.* (1983) showed that this will not necessarily influence the position of the c.m.c. of ethoxylated surfactants with a Poisson distributed polydispersity. Their analysis predicted that the c.m.c. of symmetrically distributed polydisperse samples is approximately the same as the c.m.c. of homodisperse nonionic surfactants whose ethoxy chain length corresponds to the average value of the polydisperse samples. Therefore the variation in the c.m.c. as a function of the ethoxy chain length, as has been described in section 3.3, can be attributed solely to the differences in length of the average ethoxy chain. This means that the free energy of micelle formation is also a function of the ethoxy chain. The lowering of this free energy will be large for a surfactant with a short ethoxy chain, being nearly only determined by the nature of the hydrophobic part of the surfactant, and will be small for a surfactant with a long ethoxy chain.

The width of the size distribution can be experimentally estimated for micelles of NPE. The micellar weight average molecular masses and the deduced aggregation numbers have been determined by light scattering (section 3.5). By means of surface tension measurements an aggregation number can also be measured (section 3.3). The ratios of these aggregation numbers for the different NPE surfactants have been given in table 3.12. For all surfactants values have been found which differ significantly from unity, giving a clear indication of a broad micellar size distribution, even if one takes into account the deviation described by Becher (1965).

Table 3.12 Ratios of aggregation numbers obtained by light scattering and surface tension for different Synperonic NPE surfactants at 298.15 K

| Surfactant | $m_{LS}/m_{ST}$ |
|---|---|
| NPE 1800 | 2.0 ± 0.6 |
| NPE A | 2.1 ± 0.5 |
| NPE B | 1.9 ± 0.5 |
| NPE C | 1.9 ± 0.5 |

The spatial structure of the NPE-micelles is also determined by the conformation of the polyoxyethylene chains. As discussed previously it is not likely that the hydrophobic core will be spherical. However in micelles which are composed of surfactants with long ethoxy chains, such as Synperonic NPE surfactants, the geometric restrictions imposed by the hydrophobic parts will be less reflected in the shape of the micelle (fig. 3.18). A second argument can be derived from the fact that the aggregation number decreases with increasing number of ethylene oxide units per chain. As this number of units increases the hydrophobic core will be less determining for the micellar shape. Consequently it seems to be justified to use a sphere as a first approximation for the shape for micelles of Synperonic NPE.

Polyoxyethylenes in aqueous solutions are typical randomly coiled polymers (Bailey and Kloske, 1967). One would expect the polyoxyethylene chains extending from the hydrophobic core to be likewise randomly coiled in the absence of the geometrical restrictions imposed by micelle formation. This would lead to approximately a square-root dependence of the root-mean-square end-to-end distance $R_2$ on the number of polyoxyethylene units. However the forced close packing could probably affect these preferred conformation. This problem has been considered extensively in literature, with the clear conclusion that the polyoxyethylene chains must be randomly coiled even in the micelle (Tanford *et al.*, 1977; Güveli *et al.*, 1983). This conclusion is supported by the Synperonic NPE micelles by estimating $R_2$.

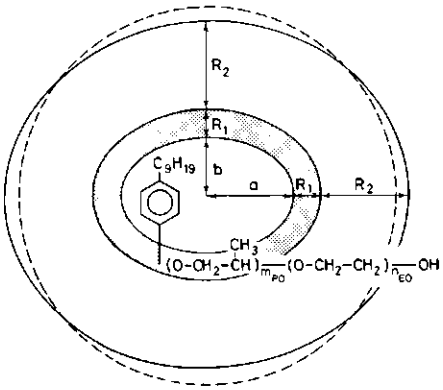


Fig. 3.18 Schematic model for a NPE micelle.
The central part represents the hydrophobic core formed by the nonylphenol part. The shaded portion represents the polypropylene sheet and the outer mantle is the part formed by the polyoxyethylene chains. The spherical geometry is given by the dashed line, the drawn outer curve applies for constant $R_2$.

The intrinsic viscosity may be converted to an effective hydrodynamic radius $R_H$ assuming a spherical shape by the equation (Tanford, 1961, 1977):

$$[\eta]M/N_{Av} = (10\pi/3)R_H^3 \qquad (3.42)$$

To calculate $R_2$ the effective hydrodynamic radius of the hydrophobic core ($R_{HC}$) should be subtracted from the total radius $R_H$. A linear extrapolation of the intrinsic viscosity to zero ethylene oxide length yields a value of $(6.3 \pm 0.3)\cdot 10^{-3}$ $m^3kg^{-1}$. This extrapolated intrinsic viscosity in its turn can be converted to an effective hydrodynamic radius of the hydrophobic core. The results are given in table 3.13 and in fig. 3.19.

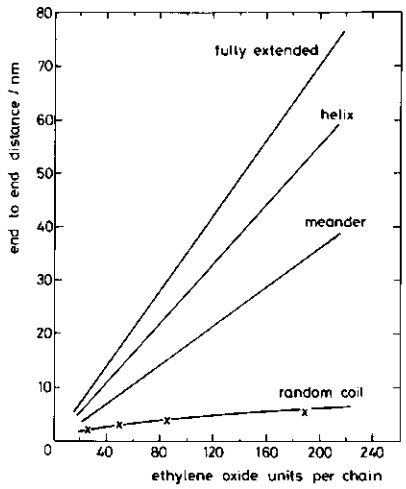


Fig. 3.19 Length of the polyoxyethylene segment as a function of ethylene oxide units per chain for several alternative conformations. X = experiments.

In this figure the end-to-end distances for four different models are plotted as a function of the number of oxyethylene units. The different models are shown in the figure. From this figure it is clear that the polyoxyethylene chains must be randomly coiled. We will come back on this result in chapter 5 dealing with the film-thickness measurements.

This conformation can be the basis for an explanation for the empirical formula 3.29 proposed by Becher in which an increasing ethoxy chain length is related to a lowering of the aggregation number. Due to this randomly coiled conformation the volume and the cross-sectional area of a monomer in the micelle will be larger as the ethoxy chain length will be larger. Hence the aggregation numbers of surfactants with short ethylene oxide chains will be larger than those of surfactants with long ethylene oxide chains. This means that the outer parts of micelles with surfactants from the latter category will be tenuous and therefore more hydrated.

Micelle hydration numbers can easily be obtained from viscosity and density data (Schott, 1967; El Eini *et al.*, 1976; Güveli *et al.*, 1983). The hydration of the Synperonic NPE surfactants varies between 2.4 g of water per g of detergent for the lowest molecular mass to 7.6 g for the highest molecular mass. This corresponds with 11.0 to 20.6 water molecules per ethylene oxide group. These larger numbers for longer chains are in accordance with the randomly coiled conformation and simply represent the typical increase in the amount of trapped solvent. This can have some consequences for the influences of various electrolytes on micellar solutions.

Table 3.13. Effective polyoxyethylene chain lenght calculated from the intrinsic viscosity.

| Surfactant | $R_2$ (nm) |
|---|---|
| NPE 1800 | 2.0 |
| NPE A | 3.0 |
| NPE B | 3.7 |
| NPE C | 5.4 |

## 3.9 Concluding remarks

Attention has been paid to the properties of Synperonic NPE surfactant solutions in comparison with other ethoxylated surfactants. The surface tension, density, heat capacity, light scattering and viscosity of these surfactants have been studied as a function of surfactant concentration and added electrolytes. It was clear that Synperonic NPE is not at variance with other ethoxylated surfactants.

APPENDIX

Table 3.3 Apparent molar volumes and heat capacities of some Synperonic NPE in water at 298.15 K

| Surfactant | $m_s$ (mmol $kg^{-1}$) | $\rho-\rho_o$ ($kgm^{-3}$) | $\phi_{v,s}$ ($dm^3 mol^{-1}$) | $\frac{\sigma-\sigma_o}{\sigma_o}$ ($\cdot 10^3$) | $\phi_{c,s}$ ($kJK^{-1}mol^{-1}$) |
|---|---|---|---|---|---|
| NPE 1800 | | | | | |
| | 5.96391 | 1.282 | 1.8874 | - 1.68 | 6.675 |
| | 12.12511 | 2.569 | 1.8897 | - 3.50 | 6.633 |
| | 18.14307 | 3.787 | 1.8896 | - 5.16 | 6.642 |
| | 24.76281 | 5.101 | 1.8896 | - 7.10 | 6.618 |
| | 31.43589 | 6.396 | 1.8895 | - 9.12 | 6.589 |
| | 37.54490 | 7.557 | 1.8895 | -11.09 | 6.552 |
| | 44.70288 | 8.870 | 1.8896 | -13.32 | 6.524 |
| | 52.00614 | 10.193 | 1.8897 | -15.36 | 6.519 |
| | 67.26790 | 12.874 | 1.8893 | | |
| NPE A | | | | | |
| | 3.13285 | 1.224 | 2.8131 | | |
| | 6.33318 | 2.408 | 2.8202 | | |
| | 9.49233 | 3.557 | 2.8225 | | |
| | 12.90226 | 4.773 | 2.8238 | | |
| | 16.35973 | 5.987 | 2.8244 | | |
| | 19.52980 | 7.065 | 2.8255 | | |
| | 23.15162 | 8.304 | 2.8252 | | |
| | 26.80855 | 9.521 | 2.8252 | | |
| | 30.48990 | 10.729 | 2.8251 | | |
| | 34.46603 | 11.999 | 2.8253 | | |
| NPE B | | | | | |
| | 2.13492 | 1.337 | 4.0785 | | |
| | 4.28508 | 2.666 | 4.0772 | | |
| | 6.51584 | 4.032 | 4.0750 | | |
| | 8.76166 | 5.379 | 4.0744 | | |
| | 11.05788 | 6.728 | 4.0744 | | |
| | 13.32115 | 8.036 | 4.0743 | | |

Table 3.3 (continued)

| Surfactant | $m_s$ (mmol $kg^{-1}$) | $\rho-\rho_o$ ($kgm^{-3}$) | $\phi_{v,s}$ ($dm^3mol^{-1}$) | $\frac{\sigma-\sigma_o}{\sigma_o}$ ($\cdot10^3$) | $\phi_{c,s}$ ($kJK^{-1}mol^{-1}$) |
|---|---|---|---|---|---|
| | 15.71935 | 9.407 | 4.0735 | | |
| | 18.18984 | 10.770 | 4.0743 | | |
| | 20.49518 | 12.162 | 4.0674 | | |
| | 23.40398 | 13.704 | 4.0690 | | |
| NPE C | | | | | |
| | 1.05528 | 1.482 | 7.9282 | | |
| | 2.14816 | 2.943 | 7.9260 | | |
| | 3.25292 | 4.440 | 7.9193 | | |
| | 4.37945 | 5.933 | 7.9178 | | |
| | 5.55444 | 7.459 | 7.9175 | | |
| | 6.66692 | 8.897 | 7.9145 | | |
| | 7.87148 | 10.400 | 7.9159 | | |
| | 9.11174 | 11.938 | 7.9148 | | |
| | 10.34534 | 13.326 | 7.9258 | | |
| | 11.77391 | 15.039 | 7.9231 | | |

Table 3.5 Apparent molar volumes and heat capacities of Synperonic NPE 1800 in some electrolyte solutions at 298.15 K

| Solvent | $m_s$ (mmol $kg^{-1}$) | $\rho-\rho_o$ ($kgm^{-3}$) | $\phi_{v,s}$ ($dm^3mol^{-1}$) | $\phi_{c,s}$ ($kJK^{-1}mol^{-1}$) |
|---|---|---|---|---|
| 0.2 M $Na_2SO_4$ | | | | |
| | 5.9668 | 26.189 | 1.8442 | |
| | 12.1070 | 27.377 | 1.8700 | |
| | 18.2500 | 28.533 | 1.8795 | 6.379 |
| | 24.8575 | 29.850 | 1.8829 | 6.348 |
| | 31.3811 | 31.038 | 1.8861 | 6.423 |
| | 37.6065 | 32.084 | 1.8881 | 6.430 |
| | 44.7957 | 33.334 | 1.8895 | 6.441 |
| | 52.1894 | 34.722 | 1.8907 | 6.448 |

Table 3.5 (continued)

| Solvent | $m_s$ (mmol $kg^{-1}$) | $\rho-\rho_o$ ($kgm^{-3}$) | $\phi_{v,s}$ ($dm^3 mol^{-1}$) | $\phi_{c,s}$ ($kJK^{-1} mol^{-1}$) |
|---|---|---|---|---|
| 0.4 M $Na_2SO_4$ | | | | |
| | 6.0338 | 50.133 | 1.7989 | 5.964 |
| | 12.2140 | 51.416 | 1.8508 | 6.317 |
| | 18.3326 | 52.502 | 1.8677 | 6.404 |
| | 25.0352 | 53.775 | 1.8792 | |
| | 31.5648 | 54.844 | 1.8837 | 6.466 |
| | 37.9131 | 55.895 | 1.8872 | |
| | 45.2705 | 57.253 | 1.8898 | 6.542 |
| | 53.0875 | 58.878 | 1.8918 | |
| 2 M NaCl | | | | |
| | 4.9184 | 78.952 | 1.8207 | 7.599 |
| | 9.9436 | 80.399 | 1.8646 | 7.085 |
| | 15.0689 | 81.163 | 1.8795 | 6.864 |
| | 20.2910 | 82.109 | 1.8871 | 6.762 |
| | 25.7744 | 83.042 | 1.8923 | 6.695 |
| | 31.2805 | 83.872 | 1.8948 | 6.635 |
| | 36.7737 | 84.866 | 1.8957 | 6.588 |
| | 40.0854 | 85.989 | 1.8969 | 6.567 |
| 4 M NaCl | | | | |
| | - | 151.270 | - | - |
| | 4.1406 | 151.272 | 1.7474 | |
| | 8.3885 | 150.723 | 1.8518 | 6.359 |
| | 12.5789 | 150.185 | 1.8861 | 6.675 |
| | 17.0170 | 149.702 | 1.8995 | 6.448 |
| | 21.4714 | 149.192 | 1.9088 | |
| | 25.6746 | 148.724 | 1.9144 | 6.421 |
| | 30.3128 | 148.236 | 1.9181 | 6.435 |
| | 35.0355 | 147.668 | 1.9232 | 6.415 |
| | 39.8521 | 147.187 | 1.9248 | |
| | 44.8139 | 146.676 | 1.9266 | 6.384 |

# 4 FLOCCULATION OF DISPERSIONS STABILIZED BY SYNPERONIC SURFACTANTS

## 4.1 Introduction

In a study of the stability of emulsions several different physical processes have to be considered. In the first place it is mostly impossible to prepare a stable emulsion without an emulsifier acting as a stabilizer. During emulsification this stabilizer must be transported to the interface where it is adsorbed. The behaviour of this stabilizer at the interface determines the stability of the total system.

Emulsions may exhibit various types of instability: *phase-inversion*, *Ostwald ripening*, *creaming*, *flocculation* and *coalescence* (Tadros and Vincent, 1983).

Phase-inversion refers to the process in which the continuous and disperse phase of an emulsion interchange. This will not be a subject of the present investigation.

The growth of larger droplets at the expense of smaller ones is known as Ostwald ripening. This phenomenon is of minor importance for the stability of paraffin-oil-in-water-emulsions, due to the low solubility of paraffin oil in water (Buscall *et al.*, 1979; Davis *et al.*, 1981).

Owing to a difference in density of the two phases creaming occurs. The emulsion separates into two layers; one layer contains a relatively dilute emulsion and the other a more concentrated one.

In the flocculation process two or more emulsion droplets come together and form a cluster. The droplets retain their individuality and the process is usually reversible: the floccules can easily be redispersed e.g. by mild agitation such as shaking. The stabilizer will stay at the interface of each droplet.

Coalescence is the process in which the emulsion droplets join as a result of the disappearance of the liquid film separating them. This process is irreversible; ultimately coalescence leads to complete separation of the components of the emulsion.

In this chapter we will concentrate on the adsorption and flocculation process. In chapter 6 coalescence will be studied. As we

shall show, flocculation and coalescence are distinct processes, obeying different laws.

Studies of adsorption and flocculation are not easily performed using emulsions for several reasons. In the first place, the surface area of the emulsion partly depends on the amount of stabilizer added. This limits the adsorption measurements to values reaching near saturation. Secondly, since emulsions are generally polydisperse, measurement of the surface area is not straightforward. Moreover, this polydispersity could complicate the turbidity or light scattering methods normally used to study flocculation.

For these reasons, model hydrophobic particles such as polystyrene (PS) latex could be more easily used to study adsorption and flocculation. As an alternative adsorbent pyrogenic silica was also used to study the effect of variation of the nature of the surface.

## 4.2 Adsorption of Synperonic surfactants

The adsorption of nonionic surfactants containing polyethylene oxide chains differs in many respect from polymer adsorption. The nonionic surfactant adsorption can usually be described in terms of a Langmuir-type equation, which generally gives a good description of adsorption of small molecules (Clunie and Ingram, 1983). This is somewhat surprising because nonionic surfactants are not small molecules but rather resemble polymers. A reasonable explanation for this behaviour can be offered from the way in which surfactant molecules adsorb onto hydrophobic surfaces, with their hydrocarbon moiety in contact with the surface and the polyoxyethylene part protruding into the solution (Ottewill, 1982). Generally it is found that the maximum amount adsorbed on hydrophilic adsorbents is two or three times larger than that for the same surfactant on a hydrophobic adsorbent (Clunic and Ingram, 1983). Reasonable explanations for the adsorption behaviour of nonionic surfactants on hydrophilic surfaces are still lacking.

Kronberg (1983) indicated that the Langmuir-type adsorption observed for nonionic surfactants on PS-latices could be due to a mutual compensation of the surfactant-solvent interaction and the difference in molecular size between the surfactant and solvent molecules.

This would imply that changing the solvent quality with respect to the polyoxyethylene part would slightly alter the adsorption behaviour of the total surfactant molecule.

The aim of our study was to investigate the adsorption behaviour of the Synperonic surfactants on different surfaces and to obtain more insight into the surfactants themselves. In this respect the adsorption of Synperonic NPE surfactants onto PS-latex and pyrogenic silica has been studied as a function of temperature and electrolyte concentration.

### 4.2.1 Adsorption onto polystyrene latex

#### 4.2.1.1 *Preparation and characterization of polystyrene latex*

Monodisperse polymer latices are relatively easy to prepare but their proper characterization and in particular their surface properties are not easy to obtain. For an extensive discussion on this subject one is referred to recent reviews (Hearn *et al.*, 1981; Piirma, 1982; Van den Hoven, 1984).

Monodisperse surfactant-free PS latices were obtained by the method of Goodwin *et al.* (1974). The styrene monomer was vacuum distilled shortly before use. Potassium persulphate was used as the initiator. Two different batches of a 4% latex dispersion were prepared following recipe A/95 (Goodwin *et al.*, 1974) to obtain latex particles with a diameter of about 200 nm. These two batches were cleaned by different techniques to remove the residual reactants and product impurities. Latex D was dialysed against distilled water for about three weeks, changing the dialysate every day until no further change in conductivity was observed. Steam stripping and ion exchanges were employed to clean latex N.

The dimensions of the latex particles were determined by electron microscopy and are given in table 4.1. For both latices the size distribution was found to be very narrow as assessed by the uniformity coefficient U, which is the ratio of the weight and number average particle diameter. The values of U are included in table 4.1, indeed indicating monodisperse dispersions. A small deviation of the expected diameter (200 nm) was found.

Surface charge densities were obtained by conductometric titration of ion-exchanged samples in a $N_2$-atmosphere (a small portion of latex D was ion-exchanged for this purpose). Graphs representing the conductivity of the system as a function of the amount of NaOH added showed two distinct kinks, which can be attributed to strongly acidic sulphate groups and to weakly acidic carboxyl groups respectively (Bijsterbosch, 1978). The surface charge densities are included in table 4.1.

Table 4.1 Characterization of the polystyrene latices

| Sample | cleaning method | number average diameter (nm) | uniformity coefficient (-) | surface charge due to strong acid groups ($mC\ m^{-2}$) | surface charge due to weak acid groups ($mC\ m^{-2}$) |
|---|---|---|---|---|---|
| D | dialysis | 226 | 1.004 | -76 | -14 |
| N | steam stripping + ion exchange | 174 | 1.006 | -47 | -34 |

Both techniques which have been used to clean the latices have their disadvantages. Due to the prolonged time periods involved in the dialysis, post-reaction changes may occur and dialysis is inefficient in removal of sparingly water-soluble species such as unreacted monomer (Hearn *et al.*, 1981). This has been observed for latex D. Even after extensive dialysis a pronounced smell of the monomer could be detected. Since this residue monomer would interfere with the spectrophotometric determination of the concentration of the remaining surfactant after adsorption, it was decided to clean latex N by steam stripping and ion-exchange. However, a disadvantage of steam stripping could be a possible increase of the rate of hydrolysis of the sulphate groups (Hearn *et al.*, 1981). This may be the reason for the differences in surface charge between the strong and weak acid groups for the two latices (table 4.1), but as the surface charge was not determined before steam - stripping no definite conclusions can be drawn. A serious disad-

vantage of ion exchange is the contamination of the latex with polyelectrolytes leached from the resin. Therefore the Dowex ion exchange resins (Dowex 1-X4 and 50WX-4) were extensively purified prior to use according to the method described by Van den Hul and VanderHoff (1968). They were used as a mixed bed resin, because this procedure gives the best result (McCarvill and Fitch, 1978).

The adsorption of Synperonic NPE 1800 onto both latices showed no significant difference. A similar result has been obtained by Bonekamp (1984) for the adsorption of polylysine on PS latices cleaned by the same procedures. Therefore it was concluded that both cleaning methods were adequate for our purposes and could be used interchangeably.

#### 4.2.1.2 *Experimental*

Surfactant solutions and latex dispersions were thermostatted separately at the desired temperature, which was usually reached within one hour. Adsorption experiments were carried out by bringing together known amounts of latex and surfactant solution in centrifuge tubes. These were firmly closed and rotated end-over-end for 16 hr. (Preliminary experiments had shown that the amount adsorbed reaches a steady value within 16 hr). As the surfactant concentrations could not be accurately determined spectrophotometrically in the uv-region due to the presence of small quantities of styrene monomers or oligomers (even after steam stripping) a colorimetric technique was adopted. The colorimetric method is based on the formation of a coloured complex of iodide with polyethylene oxide (Baleux, 1972) and has been applied successfully for different types of nonionic surfactants on an ethylene oxide base (Carrion *et al.*, 1980; Tadros and Vincent, 1980). The samples for analysis were prepared by mixing the surfactant solution with an iodine reagent (2.0% w/w KI and 0.5% w/w $I_2$ in water) in a ratio of 50:1 by volume. After exactly four minutes the optical density at 500 nm was measured. By using a calibration curve this method was found to be suitable to measure Synperonic solutions up to 30 $mgkg^{-1}$.

4.2.1.3 *Results and discussion*

Examples of adsorption isotherms of Synperonic NPE on PS latex are given in fig. 4.1. The amount adsorbed (in μmol $m^{-2}$) is plotted against the equilibrium concentration (in μM). All isotherms have a Langmuir-like appearance.

Many adsorption theories exist either for small molecules (e.g. Langmuir, 1918) or for macromolecules (see e.g. Fleer and Lyklema, 1983), but not for nonionic surfactants. Theoretical considerations of nonionic surfactant adsorption have mostly been confined to qualitative descriptions. Some quantitative theories have been developed but these are mostly based on a modified Langmuir adsorption model (Clunie and Ingram, 1983). The basic assumptions in the Langmuir theory are: only one monomolecular adsorption takes place, the adsorption is localised, lateral interaction between the adsorbed molecules is absent and there exists an equilibrium between adsorbate and solvent molecules at an interface and far in the bulk solution. This will lead to an expression for the amount adsorbed ($\Gamma$):

$$\Gamma = \Gamma_m \cdot \frac{K_e c_2}{1 + K_e c_2} \qquad (4.1)$$

where $\Gamma_m$ is the amount adsorbed at complete monolayer coverage, $c_2$ the equilibrium concentration and $K_e$ the equilibrium constant. For most adsorption studies described in the literature where equation 4.1 is used to fit experimental data, the assumptions on which the Langmuir theory is based are far from being realised. In this study no desorption could be measured either upon dilution of the equilibrium concentration, indicating that the premises of the Langmuir adsorption model are not met. Similar results have been reported by Kronberg *et al.* (1981) who measured the adsorption of NP 20 on PS latex. After adsorption for the first time and extensive cleaning of the latex afterwards, they found a lower apparent adsorption of the same surfactant when using the cleaned latex. Their conclusion was that there must still be some surfactant left on the latex surface.

Nevertheless, our adsorption data can be represented fairly well by equation 4.1 as indicated by the drawn curves of fig. 4.1. The

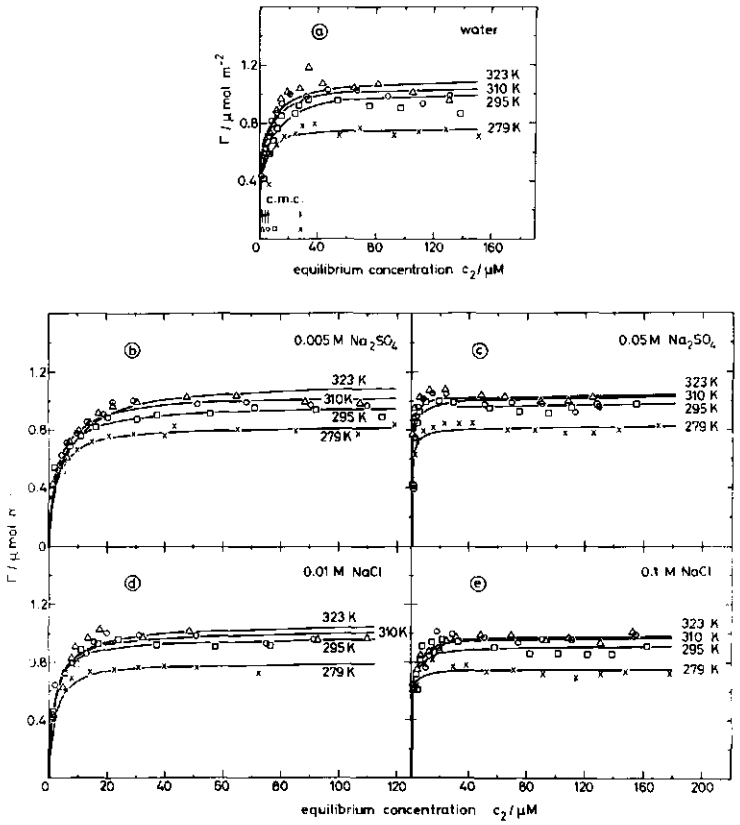


Fig. 4.1 Adsorption isotherms for Synperonic NPE 1800 on polystyrene latex. Electrolyte concentration and temperature are indicated.

values of $\Gamma_m$ for each adsorption isotherm are collected in table 4.2. In view of the absence of a full theoretical picture the value of $K_e$ obtained from fitting the data to equation 4.1 does not have a physical significance. However $\Gamma_m$ may be considered to be a satisfactory measure of the amount adsorbed in a complete monolayer.

Table 4.2 Adsorption maxima of Synperonic NPE 1800 on PS latex at different temperatures and electrolyte concentrations. The values are calculated according to equation 4.1

| Temperature | 279 K | 295 K | 310 K | 323 K |
|---|---|---|---|---|
| Solvent | ($\mu$mol $m^{-2}$) | ($\mu$mol $m^{-2}$) | ($\mu$mol $m^{-2}$) | ($\mu$mol $m^{-2}$) |
| water | 0.76 ± 0.02 | 1.03 ± 0.04 | 1.05 ± 0.03 | 1.11 ± 0.03 |
| 0.005 M $Na_2SO_4$ | 0.84 ± 0.01 | 0.97 ± 0.01 | 1.06 ± 0.02 | 1.15 ± 0.04 |
| 0.05 M $Na_2SO_4$ | 0.82 ± 0.02 | 0.98 ± 0.02 | 1.03 ± 0.03 | 1.03 ± 0.02 |
| 0.01 M NaCl | 0.81 ± 0.02 | 0.97 ± 0.02 | 1.02 ± 0.04 | 1.07 + 0.05 |
| 0.1 M NaCl | 0.75 ± 0.02 | 0.92 ± 0.04 | 0.97 ± 0.03 | 0.98 ± 0.02 |

It can also be shown from fig. 4.1 that the adsorption characteristics for NPE 1800 are similar to those of other ethoxylated nonionics reported in the literature (see e.g. Clunie and Ingram, 1983). However the adsorption plateau values of Synperonic NPE 1800 reach beyond the c.m.c. of the surfactant in the bulk solution without showing a lower adsorption plateau value before the c.m.c., as has, for example, been reported by Mathai and Ottewill (1966) for the adsorption of polyoxyethylene alkanols onto silver iodide. The lack of sensitivity of the colorimetric method may have obscured the appearance of a plateau value before reaching the c.m.c. value in this study. Alternatively the absence of a lower adsorption plateau can be attributed to a different orientation and packing of the Synperonic NPE surfactants at the surface. In general different models have been proposed for the packing and orientation of nonionic surfactants on surfaces, depending on the molecular structure of the adsorbate and adsorbent, on the concentration of the surfactant and on the solvent quality. For instance, a monolayer of vertically oriented molecules has been suggested by Ottewill and Walker (1968) for dodecyl alcohol linked to six ethoxy units on PS-latex measured by sedimentation experiments.

The orientation and packing of ethoxylated surfactants can be studied by changing the ethoxy chain length. This has been investi-

gated by Kronberg *et al.* (1981) with nonylphenol ethoxylated surfactants on PS latex. They found a decrease in the amount adsorbed expressed in μmol $m^{-2}$ with an increasing number of ethylene oxide units. The molecular cross sections on the latex surfaces appeared to be larger than those at the air/water interface. The same result has been obtained for the Synperonic surfactants in the present study. For the air/water and the paraffin oil/water interface values of 1.15 $nm^2$ and 1.22 $nm^2$ respectively were found (chapter 3), while at the latex surface a value of 1.61 $nm^2$ could be calculated at the plateau value (under the same conditions in water and at 295 K).

These high areas at the PS-water interface may be attributed to the adsorption of some of the ethylene oxide units (or some of the propylene oxide units in the case of Synperonic NPE) to the latex surface. However a complete flat monolayer coverage of NPE 1800 gives an area of about 7.0 $nm^2$ per molecule (calculated from the projection of Stuart models). This suggests that the greater part of the Synperonic molecule is not in direct contact with the surface. Most likely the results of Kronberg *et al.* (1981) and those described here can be attributed to the fact that the molecular area of the adsorbed surfactant is primarily determined by the coiling of the polyoxyethylene chain just as is the case at the oil/water and the air/water interface (chapter 3).

The differences between the results of Ottewill and Walker (1968) on the one hand and those of Kronberg *et al.* (1981) and ours on the other can probably be attributed to the difference in ethoxy chain length: smaller molecules may have a more rigid character.

Kronberg *et al.* (1981) found also that the affinity of the surfactants for the latex surfaces was strongly dependent on the ethylene oxide chain length, which for polydisperse samples would lead to preferential adsorption of the surfactants with the shorter ethoxy chain. This has been experimentally shown by Gordon and Shebs (1968), who used doubly labeled radioactive polydisperse ethoxylated dodecanol. As Synperonic NPE 1800 is also polydisperse this can lead to differences in the molecular area obtained by the various experimental techniques. Due to the weight average determination of the equilibrium surfactant ethylene oxide concentration in the

adsorption studies on PS latices, a lower maximum adsorbed number of molecules will be found than will be obtained by a number average method. This will lead to a larger molecular area. On the other hand, the molecular area of a polydisperse sample obtained from the plateau values determined by surface tension technique will be smaller, as has clearly been demonstrated by Donbrow (1975). Therefore if preferential adsorption occurs, the deviation between the molecular cross section of the Synperonic surfactant adsorbed on the latex/water interface and the air/water interface can also be attributed to the differences in the techniques employed. Unfortunately the extent of this heterodispersity effect on the surfactant adsorption on PS latex could not be independently determined since the number average and the weight average method could not be applied simultaneously.

The adsorption of NPE 1800 is temperature dependent as can be deduced from fig. 4.1 and table 4.2. It is very tempting to calculate the free energy of adsorption from the equilibrium constant and then the isosteric enthalpy of adsorption from the isotherms, using the Clausius-Clapeyron equation. This enthalpy is positive if the amount adsorbed increases with increasing temperature, implying that the adsorption is entropically driven. This is only strictly correct if the premises of adsorption equilibrium are met and if the conditions are isosteric, meaning that all other variables including the surface excess of water are independent of the temperature. This is certainly not the case, as has been described in the previous chapter for the bulk solution alone. It is likely that the conformation of the adsorbed surfactants will be subject to alterations due to temperature changes.

The experimental results (fig. 4.1) show that the adsorbed amount increases with increasing temperature. Similar results have also been reported by Harris (see Clunie and Ingram, 1983) for the adsorption of decylalcohol linked to five ethoxy groups on PS latex and by Corkill *et al.* (1966) for the adsorption of ethoxylated octyl alcohols on Carbon Black. An explanation for this temperature dependence has been suggested by the latter authors. They suggested that due to the dehydration of the ethoxylated head group with increasing temperature these groups become less hydrophilic and therefore more compact on the surface.

The effect of changing the electrolyte concentration was much less pronounced than the temperature effect. An increase in the amount adsorbed should be expected with an increase in electrolyte concentration, but in some cases even a decrease was observed. However it should be noticed that most of the changes observed were within experimental error in determining the adsorption and therefore no definitive conclusions can be drawn from these results. Unfortunately it was not possible to investigate the effect of addition of higher electrolyte concentrations which is expected to produce a significant change in adsorption. A high concentration of electrolytes causes premature flocculation of the latex which is partially covered with surfactant.

Summarizing: the above adsorption results seem to indicate that the Synperonic surfactants are adsorbed with their hydrophobic moiety on the water/latex interface with the ethylene oxide chain protruding in the solution.

### 4.2.2 Adsorption onto silica

#### 4.2.2.1 *Characterization of silica*

As the second adsorbent silica (Aerosil OX50 from Degussa, FRG) has been used. The surface of this pyrogenic silica consists of siloxane and silanol groups, of which the siloxane groups predominate. The hydrophilic properties of the silica surfaces had to be ascribed to the few silanol groups, which have a surface density of about 4 $nm^{-2}$ (Boehm, 1966). Due to this type of surface heterogeneity silica will be an interesting adsorbent for amphiphilic substances like nonionic surfactants. Hydrogen bonding will be an important adsorption mechanism for the silanol groups, while hydrophobic bonding is expected to prevail for the siloxane groups.

According to the manufacturer, Aerosil OX50 should have a surface area of $(5.0 \pm 0.1)\cdot 10^4$ $m^2kg^{-1}$. Measurements of the surface area by BET nitrogen adsorption (Carlo Erba Sorptomatic 1800, Italy) gave a value of $(6.03 \pm 0.01)\cdot 10^4$ $m^2kg^{-1}$, taking an area of 0.162 $nm^2$ per adsorbed nitrogen molecule. It is generally found in literature that heating at elevated temperatures causes a reduction in specific surface area, presumably due to a sintering

process (Rubio and Kitchener, 1976). Tadros (1978) reported that this reduction in surface area took place only at temperatures above 670 K. Besides reduction in surface area, a heat treatment also reduces the number of surface hydroxyl groups rendering the silica more hydrophobic. Therefore in order to remove any physically adsorbed water, in the preparation of the samples for the BET- and adsorption measurements a mild heat treatment was chosen (24 hours at 500 K and 2 hours at 410 K respectively under lowered pressure, with a subsequent cooling in a desiccator). This treatment does not affect the number of silanol groups on the surface (Cohen Stuart *et al.*, 1982a).

#### 4.2.2.2 *Experimental*

Silica suspensions (2.5% w/v) were prepared at room temperature. Dispersing of the dry silica powder was achieved by ultrasonication at 25 kHz (Branson PP300) for 30 min. This procedure resulted in suspensions that remained stable for several weeks.

The adsorption experiments were carried out in a similar way as described previously (section 4.2.1.1). With this system the number average surfactant concentrations could be determined spectrophotometrically using the extinction at 277 nm, because there was no interference from the adsorbent, whereas for the PS latex system a weight average concentration method was used. As described in chapter 2 (and also found by Papenhuijzen and Fleer, 1984) aggregation of surfactants can interfere with the spectrophotometric determination of the concentration. This interference has only been found for the Synperonic samples with relatively high c.m.c. values. Therefore only in the case of such high c.m.c. values calibration curves consisting of two straight lines were used. However for most Synperonic surfactants such a correction was not necessary and only one extinction coefficient has been applied.

For comparison purposes some adsorption experiments have also been performed with the Synperonic NP samples.

#### 4.2.2.3 *Results and discussion*

As the rate of adsorption is determined by several processes, the amount of NPE 1800 from water onto silica was measured after various

time intervals. The actual diffusion process of the surfactant molecules from the bulk to the interface will be fast, certainly when the solution is thoroughly mixed during the adsorption experiment. Due to the surface heterogeneity, the possibility exists that there will be some rearrangement at the surface which may be slower than the rate of supply by diffusion.

Several adsorption times for adsorbates onto silica have been reported in literature. For precipitated silica substrates usually short times (± 1 hr) were adopted because adsorption was observed to decrease rapidly with aging (Tadros, 1978). On the other hand for hydrophobic silicas adsorption times varying from 48 hours (Aston *et al.*, 1980) to one week (Seng and Sell, 1977) have been used.

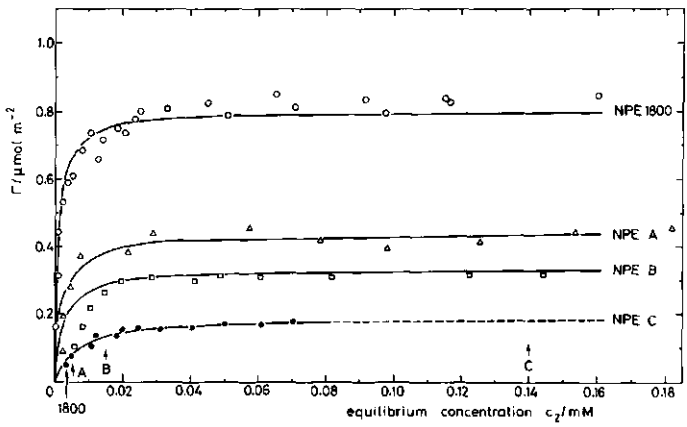


Fig. 4.2 Adsorption isotherms for different Synperonic NPE's on Aerosil OX50 at 295 K. No electrolytes added; pH = 4.7.
The drawn lines are isotherms calculated using equation 4.1.

For Synperonic NPE 1800 the amount adsorbed already reached a constant value after two hours adsorption time. For practical reasons an adsorption time of 16 hours has been chosen, similar to the adsorption experiments onto PS latex.

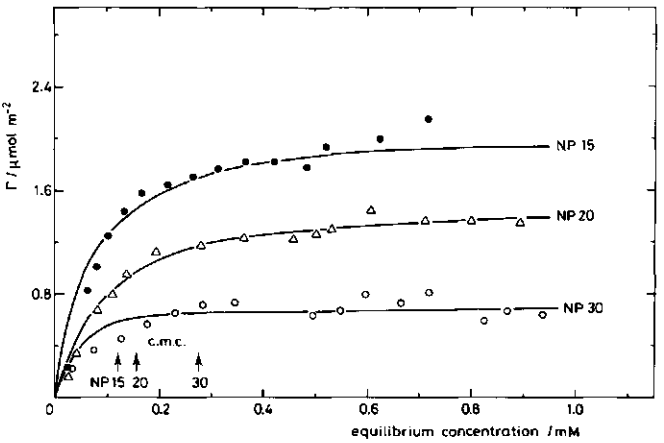


Fig. 4.3 Adsorption isotherms for different Synperonic NP's on Aerosil OX50 at 295 K. No electrolytes added; pH=4.7
The drawn lines are isotherms calculated using equation 4.1.

In fig. 4.2 and 4.3 results are shown of the adsorption of Synperonic NPE 1800 and some analogues on Aerosil OX50. The amount adsorbed (in μmol $m^{-2}$) is plotted against the equilibrium concentration (in mM). The drawn lines are the isotherms calculated according to equation 4.1. In table 4.3 the corresponding plateau values are given. As can be seen the maximum amount adsorbed decreases with increasing ethylene oxide chain length indicating that the average area per adsorbed molecule is increasing with the number of ethylene oxide groups. Similar results have been obtained for Synperonic NPE at the air/water interface (see chapter 3) and have been reported for other types of nonionics in literature (Rupprecht and Liebl, 1972; Seng and Sell, 1977; Furlong and Aston, 1982).

The adsorption characteristics for the Synperonic NP surfactants are in good agreement with the results of Furlong and Aston (1982),

which have also been obtained with ethoxylated nonylphenol surfactants on silica but with only a different number of ethoxy units.

Table 4.3 Adsorption maxima of Synperonic surfactants on Aerosil OX50 at 295 K

| Surfactant | $\Gamma_m$ ($\mu$mol $m^{-2}$) | $\sigma$ ($nm^2$ per molecule) |
|---|---|---|
| NP 15 | 2.09 ± 0.05 | 0.79 |
| NP 20 | 1.54 ± 0.05 | 1.08 |
| NP 30 | 0.72 ± 0.05 | 2.31 |
| NPE 1800 | 0.80 ± 0.02 | 2.08 |
| NPE A | 0.44 ± 0.01 | 3.78 |
| NPE B | 0.33 ± 0.04 | 5.03 |
| NPE C | 0.20 ± 0.01 | 8.31 |

The results of the Synperonic surfactants on silica bear much resemblance to the corresponding isotherms on PS-latex. The latter results suggest that the adsorption in this system is determined by interaction between the hydrophobic surface and the hydrophobic moiety of the adsorbate (see previous section). However several other factors need to be considered for interpretation of the adsorption isotherms on silica.

Seng and Sell (1977) investigated the adsorption of ethoxylated surfactants similar to the Synperonic NP series on silica (Aeroxil 200, a similar type silica as used in this study) and on some modified silicas. The latter were prepared from Aerosil 200 by esterification of the surface silanol groups with various hydrophobic compounds. These authors concluded from the cross-sectional areas in the plateaus of the isotherms, that, on unmodified silica, the adsorption is determined by interaction between the polar silica surface and the relatively polar ethylene oxide chain of the surfactant. However this conclusion can not be entirely correct for two reasons. Firstly, these authors assumed dimensions for the ethylene oxide monomer which are low by a factor of two when compared with generally accepted values (Rupprecht *et al.*, 1973; Tronel-Peyroz *et al.*, 1984) and which can be easily verified with

the well-known Stuart models. Secondly, because of their method of analysis, they were not able to measure adsorption at equilibrium concentrations above the c.m.c. As can be concluded from the results for the Synperonic NP surfactants, the maximum plateau adsorption is not always reached at the c.m.c. depending on the surfactant molecule. This will lead to an underestimation of the amount adsorbed and to a higher packing density at the interface than has been stated by Seng and Sell (1977), but this will not necessarily alter their conclusion about the way of adsorption of the surfactant on the surface. Moreover their conclusion that ethoxylated surfactants are adsorbed with their ethoxy units on the silica surface has been supported by pmr studies of Rupprecht and Liebl (1972). The latter authors found upon adsorption a change in the relaxation times of the ethoxy protons, but not of those orginating from the hydrophobic moiety. Further support for interaction between the silica surface and the ethoxy units of the surfactant can be derived from the study of Rubio and Kitchener (1976). These authors clearly demonstrated that poly(ethylene oxide) alone adsorbs onto silica. They suggested that the isolated silanol groups provide the adsorption sites, acting as proton donors in hydrogen bonding to ether oxygens. These authors also showed that the adsorption of PEO on pyrogenic silica was independent of acid pH values up to a value of pH = 6. At higher values of the pH the maximum amount adsorbed decreased rapidly with pH. Similar results were found for the adsorption of Synperonic NPE 1800 on silica as a function of the pH (fig. 4.4). The reduction of adsorption with increase of pH was explained by Rubio and Kitchener (1976) in terms of dissociation of the silanol groups on the pyrogenic surface which becomes significant above pH = 6. This results in a reduction of the number of silanol groups available for hydrogen bonding. The strikingly similar adsorption behaviour on pyrogenic silica between PEO and Synperonic NPE 1800 also suggests that the adsorption of the nonionic surfactant on silica occurs via hydrogen bonding between the ethoxy chain and the silanol groups.

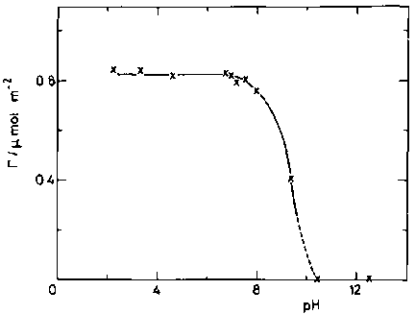


Fig. 4.4 Influence of the pH on the plateau adsorption of Synperonic NPE 1800 on Aerosil at 295 K.

The influence of electrolytes on the adsorption of ethoxylated surfactants onto silica has been studied by Rupprecht *et al.* (Rupprecht and Liebl, 1975; Rupprecht, 1978). A small increase in adsorption was found in the presence of electrolytes containing structure-forming anions and a small decrease with structure-breaking anions. Due to the competitive adsorption of some cations onto the silica surface a complicated picture emerged for the adsorption as a function of electrolyte type and concentration. Two effects can be distinguished to explain the changes in the adsorption of the surfactants. Firstly, at high electrolyte concentration the solvent quality for the surfactants can be altered, and secondly, the added electrolyte causes a change in the silica surface charge. Both effects give rise to a change in adsorption. Therefore studying the influence of electrolytes on the adsorption is not sufficient for discriminating between these two driving forces. However, the effect of changing the solvent quality can also be achieved by altering the temperature. This was studied for Synperonic NPE 1800 and the results are shown in fig. 4.5. The adsorption increases with temperature, following the same trend obtained for the adsorption on PS latex. This strongly suggests that the

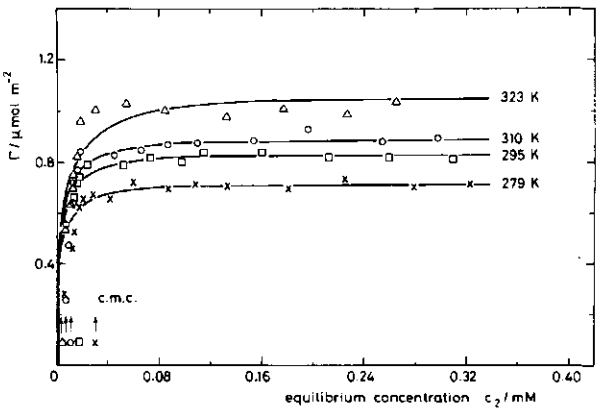


Fig. 4.5 Adsorption isotherms for Synperonic NPE 1800 on Aerosil OX50 at four different temperatures. No electrolyte added pH = 4.7.

mode of adsorption on silica is similar to that on PS latex, although the results of the adsorption as a function of the pH tend to show a different mode of adsorption on the silica-surface.

Probably a more decisive result for determining the factor responsible for adsorption is obtained with preferential adsorption experiments. If the adsorption is governed by hydrophobic interaction, the adsorption of molecules with the shorter ethoxy chain will be favoured, since all molecules will have the same adsorption energy, but will have a lower solubility in the solvent. However if the adsorption is governed by the hydrophilic moiety the reverse will be expected, i.e. the molecules with the higher ethylene oxide content will be preferentially adsorbed. With this in mind an adsorption experiment was performed on silica at two different concentrations with a mixture of Synperonic NPE 1800 and NPE C in a weight ratio of 3:1. The adsorption isotherms are given in fig. 4.6 at two silica concentrations together with the results obtained with Synperonic NPE 1800 and NPE C separately. Surprisingly a high affinity isotherm is obtained giving an intermediate plateau value of 0.58 ± 0.05 μmol $m^{-2}$. This correlates well with the theore-

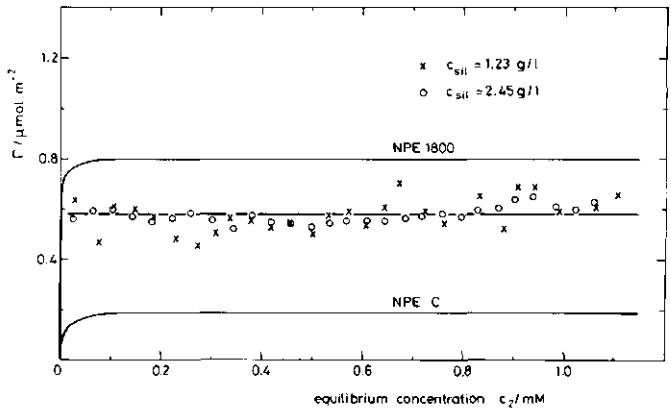


Fig. 4.6 Adsorption isotherm for a mixture of Synperonic NPE 1800 and NPE C in 3:1 weight ratio on Aerosil OX50 at two concentrations at 295 K as well as the adsorption isotherms for NPE 1800 and NPE C separately. For clearity experimental points for the latter two adsorption isotherms are omitted.

tical value of 0.62 μmol $m^{-2}$ for a mixture of this composition adsorbing without any preference for either components.

From the above results the way by which the surfactant attaches itself onto the silica surface still remains uncertain. Some additional experiments such as flocculation studies could possibly provide an answer to this problem.

## 4.3 Flocculation

### 4.3.1 General features

The change from stability to instability of a colloidal dispersion has received a great deal of attention in the literature. Stability in colloidal sense means that particles do not aggregate at a significant rate (IUPAC, 1972). The particles in a dispersion have an inherent tendency to aggregate because of Van-der-Waals attraction. Stability is achieved only if, in addition to the Van-der-Waals

attraction, there are also repulsive forces; the more these repulsive interactions outweigh the Van-der-Waals attraction, the more stable the system. Various types of repulsive forces may be distinguished. In the case of dispersions stabilized by a nonionic surfactant the repulsive force arises from the steric interactions between the adsorbed layers of the surfactant and there may also be some contribution from electrostatic repulsion. The combination of the attraction and repulsion is usually represented in terms of net energy as a function of separation between the surfaces. This energy-distance curves will be discussed in the next chapter. Anticipating this treatment for dispersions stabilized by nonionics a region of attraction is found at comparatively large distances and a region of repulsion at shorter distances, so that the potential energy diagram shows a minimum at a certain distance from the particle surface (see fig. 4.7). When this minimum is shallow the system will be stable. This interaction between adsorbed layers is the so-called steric stabilization or adsorption stabilization (Scheutjens and Fleer, 1982). The boundary between stability and instability is somewhat arbitrarily defined. Since particles are subject to Brownian motion, even in the absence of convection, encounters will always occur. When the depth of the minimum is less than about 1 kT the system will be considered as

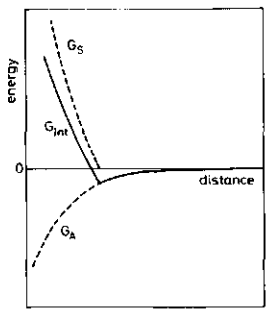


Fig. 4.7 Interaction energy ($G_{Int}$) for two identical particles stabilized by adsorbed nonionics, due to steric repulsion ($G_S$) and Van-der-Waals attraction ($G_A$). Highly schematic.

"stable". Complete flocculation may be taken to correspond to the situation where the lifetime of aggregates is infinite and there will be effectively zero concentration of singlet particles. This flocculation may take place when the depth of the minimum is more than 5 kT, although this is also somewhat arbitrary (Vincent, 1983). Between these two boundaries a transition region exists. In this region flocculation will take place at a given depth of the minimum when the particle volume fraction or particle size exceeds a critical value (Long *et al.*, 1973; Vincent, 1983). Several other factors also play some role in determining the stability of a dispersion. Firstly, to ensure good stability there should be complete coverage of the particle interface by the adsorbed surfactant. In the case of an emulsion the presence of a sufficient amount of stabilizer is even a prerequisite, otherwise the emulsion can not be prepared (see chapter 6). Under conditions of incomplete coverage of a solid surface, chains protruding from the surface of one particle may be attached to the surface of a second particle leading to bridging flocculation or adsorption flocculation (Scheutjens and Fleer, 1982). A second factor in determining stability is the effective thickness of the adsorbed layer which should be high enough to render the depth of the minimum neglibly small. Since the Van-der-Waals attraction is dependent on particle size, large particles require thicker adsorbed layers than small particles for producing the same stability (Ottewill and Walker, 1974; Cowell and Vincent, 1982b). Thirdly, addition of non-adsorbing polymers to a sterically stabilized dispersion can, under some conditions, lead to depletion flocculation depending on the concentration and molecular weight of the added polymer (Li-In-On *et al.*, 1975; Cowell *et al.*, 1978; Vincent *et al.*, 1980; Feigin and Napper, 1980a, b; Scheutjens and Fleer, 1982; Fleer *et al.*, 1984).

In the present investigation the above mentioned factors namely complete coverage, effective thickness of the adsorbed layer and the addition of non-adsorbing polymers, were kept constant unless otherwise stated.

Flocculation was induced by reducing the solvent quality for the stabilizing moiety, so that the interaction between surfactant layers adsorbed on different particles eventually becomes attractive. This may be achieved through temperature changes or through

the addition of a non-solvent for the stabilizing chain (Napper, 1977). When the solvency is gradually reduced, a very sharp transition from long term stability to fast flocculation is usually observed, so that a sharp stability criterion can be experimentally defined. The critical point at which flocculation is first observed is referred to as the *critical flocculation temperature* (c.f.t.) (for temperature alteration) or the *critical flocculation concentration* (c.f.c.) (in the case of addition of electrolytes). As a rule this type of flocculation is reversible i.e. the system redisperses spontaneously when the conditions are reversed.

Flocculation studies can be carried out using a number of techniques of which light scattering is the most commonly used (Ottewill and Shaw, 1966). Some of these techniques will be discussed in the following section.

### 4.3.2 Experimental

#### 4.3.2.1 *Sample preparation*

Surfactant solutions were added to the dispersion in concentration corresponding to the plateau region of the adsorption isotherms. The latter were established previously as discussed in section 4.2. Enough time was allowed for adsorption equilibrium to be achieved. To ensure that actual flocculation of the particles and not just a turbidity change arising from the surfactant phase separation was monitored whenever the cloud point of the surfactant solution was reached, a reference sample was used by centrifuging a portion of the dispersion to obtain a particle free supernatant.

Emulsions were prepared in the following way. A dilute emulsion was left to cream under action of gravity (experimental details of the emulsion preparation will be given in chapter 6). The cream layer was discarded and the substratum was used for the flocculation experiments. As it appeared impossible to prepare a nearly droplet-free solution of this substratum a diluted surfactant solution was used as reference.

4.3.2.2 *Flocculation tests*

Flocculation experiments were performed using various methods. In the first method the particle size of an originally homodisperse latex dispersion was measured as a function of electrolyte concentration at a fixed temperature using a Nanosizer (Coulter Electronics Ltd. UK) following the method of Tadros and Vincent (1980). Essentially the apparatus determines the average diffusion coefficient D of the particles by measuring the intensity fluctuations of the scattered He-Ne laser light at an angle of 90° as the particles undergo Brownian motion (Pusey, 1973). From the average diffusion coefficient an average effective particle diameter ($d'_{eff}$) is calculated using the Stokes-Einstein equation:

$$D = k_B T / 3\pi\eta d'_{eff} \qquad (4.2)$$

where the other symbols have their usual meaning. As the instrument was not provided with a thermostatted cell, only c.f.c. at room temperature could be measured.

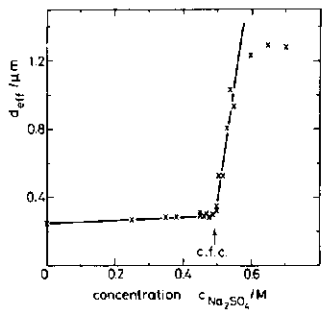


Fig. 4.8 Critical flocculation electrolyte concentration (c.f.c) for $Na_2SO_4$ at 294 K of a PS latex system stabilized by Synperonic NPE 1800 assessed using a "Nanosizer".

The obtained $d'_{eff}$'s were plotted versus the electrolyte concentration. The concentration corresponding with the intersection of the horizontal and ascending branch was taken as c.f.c. An example of such a plot is given in fig. 4.8.

The second method is based on the technique of Long *et al.* (1973), which has been further elaborated by Cowell *et al.* (1978) and Lambe *et al.* (1978). Samples of varying electrolyte concentration (below the flocculation concentration at room temperature) and a fixed particle volume fraction were prepared. No flocculation of any of the dispersions was observed at this stage. The samples were placed in a thermostatted cell of a spectrophotometer. The temperature was raised by selected small increments. After each temperature increase the samples were allowed to stand at the new temperature for 30 minutes. The turbidity was measured at each temperature as a function of the wavelength over the range 400-600 nm. From the slope n of a log (turbidity) versus log (wavelength) plot, the average particle size of the dispersion can be calculated (Long *et al.*, 1973). Since this slope is very sensitive to small changes in the average particle size, this technique is very susceptible for detecting low levels of flocculation. A typical example of such a n-versus-T plot for locating the c.f.t. is shown in fig. 4.9. At the c.f.t. a sharp break in the curve occurs.

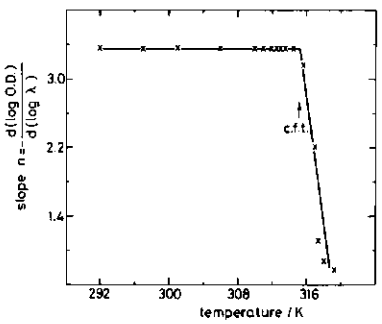


Fig. 4.9 Critical flocculation temperature (c.f.t.) of a PS latex system stabilized by Synperonic NPE 1800 in the presence of 0.4 M $MgSO_4$ assessed by the turbidity-wavelength scan method.

The third flocculation method is also based on turbidity measurements at one wavelength. Since turbidity is a function of particle

size (Kerker, 1969) changes in particle size due to aggregation can be monitored by measuring changes in turbidity (Napper, 1970; Tadros and Vincent, 1980). The experiments were carried out using a spectrophotometer combined with a temperature programming unit. The temperature was raised at 1 $K \cdot min^{-1}$. The turbidity at a fixed wavelength (670 or 540 nm) and the temperature of the dispersion were measured simultaneously and the results were displaced using a chart recorder fitted with two pens. A particle free supernatant of the same dispersion was used as the reference. The c.f.t. was assumed to correspond to the temperature at which a sharp increase in turbidity was observed. Using this procedure the c.f.t. could be located within a 0.5 K range.

For the silica dispersions, the flocculation was followed using a classical technique. An electrolyte solution was added to a well-stirred silica suspension, which after stirring was left to stand for 1 hour. The optical absorbance of a sample of the supernatant was then determined and compared with that of a control to which no electrolyte was added. As stability criterion the relative absorbance $A_r$ (defined as the quotient of the absorbance of the test sample and that of the control) was used. A relative absorbance of 1.0 indicates complete stability whereas strong flocculation is indicated by a low value of $A_r$.

### 4.3.3 Results and discussion

As in dispersions stabilized by nonionics flocculation depends upon the particle volume fraction (Long *et al.*, 1973; Cowell *et al.*, 1978; Cowell and Vincent, 1982; Edwards *et al.*, 1984) the latter has to be standardized. A critical particle volume fraction exists below which the system is stable, and above which flocs appear to be in equilibrium with singlet particles. Long *et al.* (1973) suggested that this phenomenon is in some respect analogous to a phase change. From the observed *critical flocculation volume fraction* (c.f.$\phi$), these authors were able to calculate the Gibbs free energy of the minimum, by using a Boltzmann relationship between singlets and large aggregates and by making some assumptions concerning the floc structure. Values of the Gibbs free energies determined in this way were in reasonable agreement with

those obtained by direct calculation of the interparticle interaction energies. (Long *et al.*, 1973). According to this model one may expect the c.f.$\phi$. to be temperature dependent. In addition, the c.f.t. of a sterically stabilized dispersion should be particle volume fraction dependent. The latter dependence has been clearly demonstrated by Cowell and Vincent (1982) for a sterically stabilized dispersion. For the c.f.t. they found a decreasing function of the particle volume fraction. In analogy with the vapor-condensed phase equilibrium, the c.f.$\phi$. should be an increasing function of temperature. This was experimentally confirmed for a PS-latex system stabilized with Synperonic NPE 1800 although the trend is not very pronounced. This dependence must be taken into account for the determination of the c.f.t. as a function of electrolyte concentration. Therefore, in all experiments a sufficiently low particle volume fraction was used at the lowest temperature examined.

Table 4.4 Critical flocculation particle volume fraction (c.f.$\phi$.) as a function of temperature for PS latex stabilized with Synperonic NPE 1800 in an aqueous 0.1 M $MgSO_4$ solution.

| temperature K | particle volume fraction |
|---|---|
| 299 | $(3.3 \pm 0.3)\cdot 10^{-4}$ |
| 313 | $(3.3 \pm 0.3)\cdot 10^{-4}$ |
| 331 | $(4.2 \pm 0.3)\cdot 10^{-4}$ |

In order to compare the different flocculation methods, the c.f.t.'s for one electrolyte were determined using the different techniques. The result for 0.4 M $MgSO_4$ following the method of Long *et al.* (1973) has already been given in Fig. 4.9. The critical flocculation electrolyte concentration (c.f.c.) was determined at 294 K giving a value of 0.56 M $MgSO_4$. Several c.f.t.'s were also obtained from measurement of the turbidity as function of the temperature at one wavelength following the method of Napper (1970) and Tadros and Vincent (1980). The results of these different methods are collected in fig. 4.10, together with the theta conditions for poly(ethylene oxide) obtained by Boucher and Hines (1976).

Comparing the results two conclusions can be drawn. Firstly the results are independent of the flocculation test used and secondly the c.f.t. of PS latex dispersions stabilized with Synperonic NPE 1800 coincide with the theta conditions for PEO within experimental error. This latter conclusion will be discussed later on in more detail.

Since the results of the different methods coincided it was decided to choose the most convenient flocculation test, viz. measuring the change in turbidity as a function of temperature. This method was employed throughout this study unless otherwise stated. The c.f.t.'s for PS latex dispersions stabilized with Synperonic NPE 1800 in different electrolyte concentrations are given in fig. 4.11 and in table 4.5, together with the theta conditions for PEO obtained by Boucher and Hines (1976). For all the electrolytes studied it can be concluded that the c.f.t.'s coincide with the PEO theta conditions.

Similar results have been reported by Napper (1970) for PEO coupled with various anchor polymers at full coverage on different polymer latices. However Cowell *et al.* obtained flocculation well below the theta conditions. The difference between the two studies can

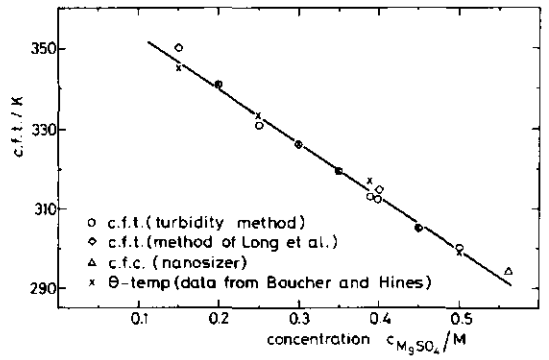


Fig. 4.10 Critical flocculation temperatures of a PS latex system stabilized by Synperonic NPE 1800 assessed by various techniques and theta temperatures of PEO taken from Boucher and Hines (1976).

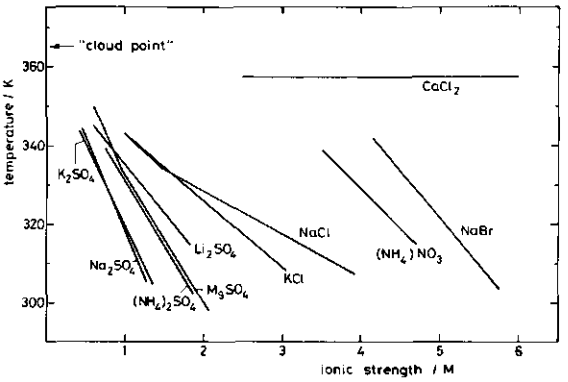


Fig. 4.11 Dependence of the c.f.t. of PS latex systems stabilized by Synperonic NPE 1800 on the nature and concentration of the electrolyte.

be attributed to the difference in the systems used by the two groups. The work of Napper (1970) has been carried out with terminally anchored stabilizing chains of relatively high molecular mass ($M > 10$ kg $mol^{-1}$). In this case repulsion is due to a thick adsorbed layer, so that the contribution from the Van-der-Waals attraction is very small and therefore flocculation is solely due to a change in the steric forces. However if this stabilizing layer is not thick enough, changes in temperature and electrolyte concentration can induce changes in the total free energy of the system, either through alterations of the thickness or the Hamaker function of the adsorbed layer (Thompson and Pryde, 1981; Vincent and Whittington, 1982). This can lead to flocculation below the theta conditions as observed by Cowell *et al.* (1978). The last mentioned authors investigated aqueous PS latex particles with incorporated PS-PEO comb stabilizers. The terminally anchored PEO chains were of relatively low molecular mass ($M = 0.75$ or 2 kg $mol^{-1}$). These dispersions flocculated under better than theta conditions although it was found that the longer the PEO chain, the closer the c.f.t. approached the theta temperature.

Table 4.5 Critical flocculation temperatures for PS latex stabilized with Synperonic NPE 1800 in various aqueous electrolyte solutions and theta temperatures of PEO

| NaCl | | | KCl | | | $MgSO_4$ | | | $K_2SO_4$ | | | $Li_2SO_4$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| conc. (M) | c.f.t. (K) | Θ (K) | conc. (M) | c.f.t. (K) | Θ (K) | conc. (M) | c.f.t. (K) | Θ (K) | conc. (M) | c.f.t. (K) | Θ (K) | conc. (M) | c.f.t. (K) | Θ (K) |
| 1.0 | 343.0 | 349 | 0.8 | 348.0 | 352 | 0.10 | >363 | - | 0.15 | 342.6 | 347 | 0.20 | 344.4 | 352 |
| 1.2 | 329.0 | 346 | 1.0 | 343.5 | 346 | 0.15 | 350.0 | 345 | 0.175 | 339.2 | 343 | 0.25 | 341.0 | 345 |
| 1.5 | 334.0 | 340 | 1.3 | 338.5 | 340 | 0.20 | 341.0 | 341 | 0.19 | 337.5 | 341 | 0.30 | 338.5 | 340 |
| 1.8 | 331.0 | 337 | 1.5 | 334.8 | 335 | 0.25 | 331.1 | 333 | 0.20 | 336.5 | 338 | 0.35 | 334.0 | 335 |
| 2.0 | 328.8 | 334 | 1.8 | 330.0 | 331 | 0.30 | 326.2 | 326 | 0.25 | 330.8 | 332 | 0.40 | 330.0 | 330 |
| 2.4 | 324.0 | 327 | 2.0 | 326.2 | 327 | 0.35 | 319.6 | 320 | 0.30 | 324.6 | 325 | 0.45 | 327.0 | 326 |
| 2.6 | 321.8 | 325 | 2.4 | 319.4 | 321 | 0.40 | 312.4 | - | 0.36 | 316.8 | 317 | 0.50 | 323.0 | - |
| 2.8 | 319.5 | 323 | 2.7 | 314.6 | 318 | 0.39 | 313.0 | 317 | 0.40 | 311.2 | 313 | 0.55 | 319.0 | - |
| 3.0 | 317.5 | 319 | 3.0 | 309.8 | 310 | 0.40 | 313.0 | - | 0.45 | 305.0 | 307 | 0.60 | 315.0 | - |
| 3.2 | 315.6 | | 3.2 | 307.0 | 308 | 0.45 | 305.6 | 305 | | | | | | |
| 3.4 | 313.2 | | | | | 0.50 | 300.0 | 299 | | | | | | |
| 3.6 | 311.2 | | | | | | | | | | | | | |
| 3.8 | 308.9 | | | | | | | | | | | | | |

| $Na_2SO_4$ | | | $(NH_4)_2SO_4$ | | | $(NH_4)NO_3$ | | | $CaCl_2$ | | | NaBr | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| conc. (M) | c.f.t. (K) | Θ (K) | conc. (M) | c.f.t. (K) | Θ (K) | conc. (M) | c.f.t. (K) | Θ (K) | conc. (M) | c.f.t. (K) | Θ (K) | conc. (M) | c.f.t. (K) | Θ (K) |
| 0.15 | 344.0 | 346 | 0.25 | 338.4 | 344 | 3.6 | 337.0 | 344 | 0.5 | 358 | 358 | 4.25 | 339.4 | - |
| 0.20 | 337.4 | 340 | 0.30 | 334.0 | 338 | 3.8 | 332.8 | 339 | 1.0 | 356 | 355 | 4.75 | 327.4 | - |
| 0.25 | 329.6 | 334 | 0.35 | 329.8 | 332 | 4.0 | 329.2 | 336 | 1.5 | 357 | 357 | 5.00 | 321.4 | - |
| 0.30 | 323.4 | 325 | 0.40 | 325.6 | 326 | 4.4 | 318.4 | 325 | 2.0 | 358 | 359 | 5.75 | 303.4 | - |
| 0.32 | 320.8 | 322 | 0.45 | 319.8 | 320 | 4.8 | 315.8 | - | | | | | | |
| 0.35 | 317.0 | 318 | 0.50 | 316.0 | 314 | | | | | | | | | |
| 0.40 | 308.8 | 310 | 0.55 | 310.6 | - | | | | | | | | | |
| 0.45 | ~ 299 | 301 | 0.60 | 305.0 | - | | | | | | | | | |

In order to study the influence of the length of the PEO tail upon stability, the c.f.t. of Synperonic surfactants, containing different numbers of ethoxy groups, was studied as a function of electrolyte concentration. From the results of Synperonic NP (fig. 4.12) it can be shown that the c.f.t. approaches the theta temperature of PEO more clearly on increasing the length of the ethylene oxide moiety.

Some other interesting features emerge from fig. 4.12. Firstly, comparing c.f.t. results for Synperonic NP 30 and Synperonic NPE 1800, it must be concluded that the stability is not only determined by the PEO moiety of both types of surfactant containing roughly the same amount of ethylene oxide units. Therefore, the propylene oxide part of Synperonic NPE 1800 must make some contribution to the stability. It may well be that the PPO moiety is not entirely on the surface, but is partly protruding in the aqueous phase. Secondly, from the similarity of the results for Synperonics NPE 1800 and NPE C, it can be deduced that elongation

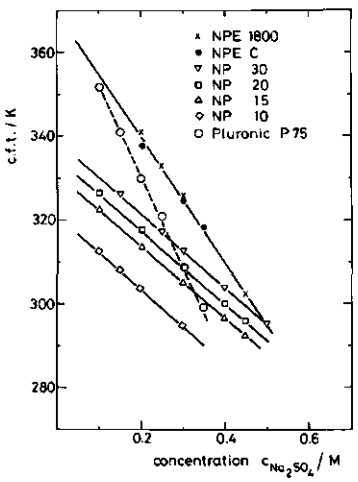


Fig. 4.12 Critical flocculation temperatures for PS latex stabilized by different adsorbed Synperonic surfactants in the presence of varying concentrations of $Na_2SO_4$. For comparison data for Pluronic P 75 are included (Tadros and Vincent, 1980).

of the ethoxy chain of Synperonic NPE 1800 does not enhance the stability. Thirdly, the slopes for all the Synperonic NP's are nearly identical but deviate from those of the theta temperature and Synperonic NPE's. Thus, by reducing the solvency through the addition of electrolytes, the c.f.t. can be lowered. The slope of the c.f.t.-electrolyte concentration yields some information on the salting-out phenomenon of the solvated part protruding in the aqueous phase. However, it is surprising to find a lower value of the slope for the Synperonic NP series when compared with that of the Synperonic NPE series. No satisfactory explanation can be offered yet.

The flocculation conditions of a physically adsorbed PEO-PPO-PEO block copolymer (Pluronic surfactant) have been investigated by Tadros and Vincent (1980). For comparison their data have also been included in fig. 4.12. Dispersions stabilized with these Pluronic surfactants are relatively less stable towards the addition of a high concentration of electrolyte than both types of Synperonic surfactant. This probably reflects a stronger reduction of the solvent quality of the medium or a difference in packing conditions for propylene oxide. As has been suggested by Cowell and Vincent (1982) a correlation between the c.f.t. and the theta

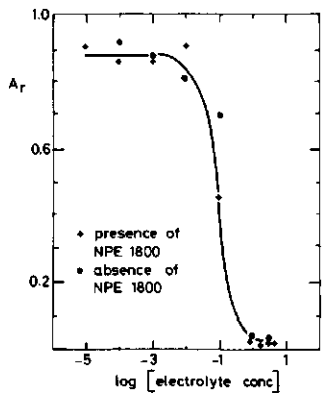


Fig. 4.13 Influence of NaCl on the flocculation of Aerosil OX50 suspension at pH 4.4 in the absence (.) and presence (+) of Synperonic NPE 1800.

conditions might be strongly dependent on the configuration and the coverage of the stabilizing moieties. Therefore the difference in stability between dispersions stabilized with Synperonic NPE and Pluronic surfactants could be due to difference in adsorption behaviour orginating from the difference in their molecular structure. More information on the effect of electrolytes on the stabilizing moieties is needed for further analysis of these trends.

The above mentioned flocculation study strongly supports the view that the Synperonic surfactants are adsorbed with their hydrophobic moiety onto the latex surface and the ethoxy chain dangling in the aqueous phase.

Flocculation studies of pyrogenic silica stabilized by Synperonic NPE 1800 did no show any effect of the adsorbed surfactant on the stability of the dispersion (fig. 4.13). As the influence of electrolytes on the adsorption of ethoxylated surfactants onto silica is small (Rupprecht, 1978), these flocculation results could suggest that the adsorption is determined by interactions between polar surface groups and the relatively polar ethylene oxide moiety of

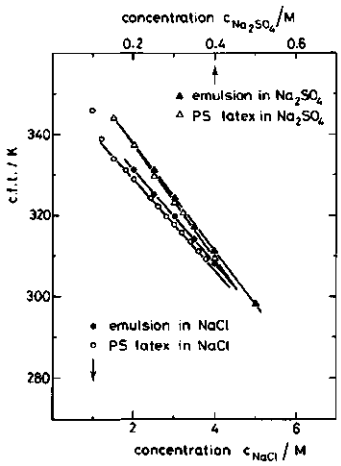


Fig. 4.14 Critical flocculation temperatures for O/W emulsions (filled symbols) and PS latex (open symbols), stabilized by Synperonic NPE 1800 in the presence of $Na_2SO_4$ and NaCl.

the adsorbate. A similar conclusion has been drawn by Papenhuijzen and Fleer (1984) for the adsorption of Synperonic NP surfactants on poly (oxy methylene) crystals. However, since the adsorption of Synperonic NPE 1800 increases with temperature (fig. 4.5) and since the adsorption characteristics show a remarkable similarity with the adsorption of the same surfactant onto PS latex, no definite conclusions can be drawn for the interaction of the ethoxylated surfactant and the silica surface.

Although no adsorption studies were performed on emulsions, the results of fig. 4.14 show that the flocculation behaviour of emulsions stabilized with Synperonic NPE 1800 is identical to that of PS latex stabilized with the same surfactant. This identity indicates that the ethylene oxide part protrudes into the aqueous phase.

## 4.4 Concluding remarks

The adsorption of Synperonic surfactants on PS latex and pyrogenic silica has been studied, together with the flocculation of dispersions stabilized with these surfactants. The adsorption behaviour of the surfactants was found to depend on the nature of the adsorbent, which had consequences for the stability of the dispersions. Polystyrene latex and emulsions could be stabilized with Synperonic NPE surfactants in saline solutions, whereas pyrogenic silica could not. The PS latex and emulsions stabilized with Synperonic NPE flocculated under theta conditions for poly(ethylene oxide) indicating that the ethylene oxide moiety of the surfactants protrudes into the aqueous solution.

# 5 THIN LIQUID FILMS OF SYNPERONIC SURFACTANTS

## 5.1 Introduction

For a long time, the various phenomena involved in the formation of soap films and in particular their thinning and stability, have been studied by many scientists. The study of these liquid films is thought to date from the time of Newton (see e.g. Iseberg, 1978). In more recent years, thin liquid films have been used as a tool for the study of colloidal stability (Lyklema, 1962). The factors which determine the stability of hydrophobic colloidal systems such as emulsions also govern the stability of liquid films. To gain more insight into some of the factors which affect emulsion stability, studies of liquid films might be very useful.

Equilibrium thickness measurements of liquid films, made from ionic surfactants were used to study double layer repulsion and Van-der-Waals-attraction (Mysels *et al.*, 1959; Overbeek, 1960; Lyklema, 1962; Duyvis, 1962; Lyklema and Mysels, 1965; Sheludko, 1967; Bruil, 1970; de Feijter, 1973; Donners, 1976). Only a few studies appear to have been carried out on thin liquid films from materials other than ionic surfactants. Musselwhite *et al.* (1967, 1968) and Graham and Phillips (1976) reported measurements of free liquid films of proteins. These measurements are difficult to perform and the interpretation of the results is tricky. Studies of liquid films of polyelectrolytes are even more scarce in literature. Only Lyklema and Van Vliet (1978) reported measurements of liquid films of PMA-pc, a copolymer of poly(methacrylic acid) and its methylester. Studies of nonionic polymer stabilized films are also rare. As far as the present author is aware only a few measurements have been reported for poly(vinylalcohol) (PVA) films by Sonntag *et al.* (1976, 1977, 1979) and by Lyklema and Van Vliet (1978). The latter authors measured equilibrium film thickness as a functon of hydrostatic pressure for three PVA-samples varying in molecular mass and nature of the distribution of the acetate groups. From these experimental measurements and theoretical calculations of the Van-der-Waals-force, the authors were able to quantify a steric repulsion force. Comparison of these results with calculations based on the theory of Hesselink *et al.* (1971)

led them to the conclusion that this repulsive force must originate from a few long polymer tails. This conclusion is also in agreement with the polymer adsorption theory of Scheutjens and Fleer (1979, 1980, 1982, 1984). Van Vliet and Lyklema concluded also that for films stabilized by PMA-pc, the polyelectrolyte molecules tend to adsorb with fewer long tails, and this agrees well with a more recent polyelectrolyte adsorption theory (Bonekamp *et al.*, 1983; Van der Schee, 1984; Van der Schee and Lyklema, 1984). The results of Sonntag (1976, 1977) for PVA differ from those of Lyklema and Van Vliet (1978) in that the former authors observed a much smaller dependence of the thickness on the hydrostatic pressure. Van Vliet (1977) attributed this discrepancy to the use of different PVA samples. Differences with respect to the addition of electrolytes may also have played a role.

Only a few studies are known for liquid films formed from nonionic surfactants. However, all the measurements reported have been performed with different types of surfactants, the techniques used are different and different additives have been used. Therefore a comparison between the various results is difficult. Below some of the reliable measurements on nonionic surfactants are reviewed.

Clunie *et al.* (1970) measured the thickness of films stabilized by n-decylmethyl sulphoxide (DMS) as a function of the surfactant concentration, added electrolyte and temperature. They obtained stable films only above the c.m.c. The equilibrium film thickness was found to be independent of surfactant concentration (up to 1.5 times the c.m.c.) and small variations in the temperature (from 298 to 308 K). The film thickness was also independent of a sodium chloride concentration up to a certain critical value above which there was a sharp increase in the film thickness with further increase in NaCl concentration. When the latter concentration was still more increased the film thickness was found to decrease gradually and eventually it reached the initial equilibrium thickness in the absence of electrolyte. This initial sharp increase was attributed to ion absorption resulting in the formation of a charged film which as an extented double layer. However, at higher concentrations of electrolytes the double layer is compressed resulting in a reduction in film thickness (Clunie *et al.*, 1970).

Buscall *et al.* (1975, 1976) studied the equilibrium thickness of films stabilized by different nonionics. The results followed the same trend as that obtained with DMS in the presence of NaCl, but in the presence of small quantities of KCNS stable thick films were formed. The thickness decreased with increasing KCNS concentrations. Similar trends have been observed for films stabilized by decyldimethylphosphine oxide (DDPO) in the presence of NaCl and KCNS. Buscall *et al.* ascribed these phenomena to ion binding, but the mechanism of this process was not completely understood.

Exerowa *et al.* (1979) investigated the equilibrium thickness of films stabilized by nonionic surfactants (NP 20, $C_{12}(EO)_{11}$ and DMS) as a function of the surfactant concentration. After reaching a steady value at relatively high concentrations a decrease in thickness was found. This seems to be in contrast with the results of Bruil (1970) using the surfactant OP 11 (which is an octylphenol with 11 ethoxy groups), similar to NP 20. The last mentioned author found neither an effect of variation in surfactant concentration nor an effect of addition of NaCl, $MgCl_2$ and $La(NO_3)_3$ on the equilibrium thickness. However Scheludko (1970) has already pointed out that a variation in the outer pressure applied to a film, could cause a difference in film thickness. This could account for the difference between these two studies. The outer pressure in the work of Bruil had a constant value of 50 $Nm^{-2}$, but the outer pressure applied by Exerowa was variable depending on the surfactant concentration. The variation in equilibrium thickness was explained by Exerowa as probably due to an electrostatic disjoining pressure. This was almost absent in the study of Bruil.

Paluch (1980) measured the equilibrium film thickness of OP 9 (which is very similar to OP 11 in the work of Bruil) as a function of the surfactant concentration using the same outer pressure as reported by Bruil. However she was able to measure equilibrium film thicknesses at much lower surfactant concentrations with the same technique as that used by Bruil and she found at these concentrations that the film thickness was much higher. By increasing the surfactant concentration the film thickness decreased until a steady value was reached which was nearly equal to that reported by Bruil. No adequate explanation for this decrease at higher surfactant concentration could be offered by Paluch (1980).

A slightly different system has been investigated by Sonntag *et al.* (1966, 1970). They measured a thin liquid film of the nonionic NP 20 between two oil droplets. A slight decrease in equilibrium thickness by increasing the surfactant concentration was observed but a more pronounced decrease was found when the electrolyte concentration was increased. The same results were also obtained by Herrington *et al.* (1982) for NP 20, although the latter authors reported that for sucrose monolaurate the equilibrium thickness increased with increase of the surfactant concentration. According to Herrington *et al.* this should be due to the rigidity of the sucrose molecules. Increase of the electrolyte concentration also produced a decrease in equilibrium film thickness for these sucrose surfactants.

Summarizing, some conclusions may be drawn form the studies of liquid films stabilized by nonionics. In the first place there is a pronounced effect of the surfactant concentration on the film thickness. At concentrations much higher than the c.m.c. thin films are formed. These films are usually referred to as Newton black films (NB-films). Secondly, although nonionics themselves are not charged, electrostatic forces do seem to play a role in the film interaction. Equilibrium films whose thickness depends on the electrolyte concentration are usually referred to as Common black films (CB-films) by some authors in analogy to films formed from ionic surfactants. Since the transition from CB-films to NB-films stabilized by nonionic surfactants is not very sharp, it may not be possible to distinguish the two types of film. Thirdly, the outer pressure applied to films can be important particularly when considered in combination with the first two mentioned effects.

The influence of addition of electrolytes on the film thickness appears to be not very unambiguous. In view of our experiments with nonionic micelles in saline solution (chapter 3) the possibility must not be excluded that the effect of electrolytes is different in different regions of concentration and that it depends on the nature of the electrolyte.

Some authors have suggested that preferential absorption of one of the ionic species in the surfactant layers seemed to be the

most logical effect. This ion absorption could create a double layer and hence would result in an increase in the film thickness. The double layer formed could be compressed by further increase in electrolyte concentration. However other authors reported no effect of electrolyte concentrations on the equilibrium thickness of films stabilized by nonionic surfactants. To date no systematic studies of te effect of electrolytes on the thickness of films formed from nonionic surfactants have been carried out. This is the subject of the present chapter where free liquid films stabilized by Synperonic surfactants have been investigated at high electrolyte concentrations and at various temperatures. Moreover, the effect of the ethoxy chain length was studied.

## 5.2 Interaction forces in free liquid films

It is generally accepted that several forces of molecular origin operate in thin liquid films, the balance of which (expressed as a pressure) determines the equilibrium film thickness. The net force is usually referred to as the *disjoining pressure* ($P_D$). This disjoining pressure is positive when it resists film thinning, whereas a negative disjoining pressure leads to film instability. For an equilibrium film this disjoining pressure is equal and opposite to the *hydrostatic pressure* ($P_H$) and to the *externally applied pressure* ($P_{EA}$).

$$P_D\,(d_e) + P_H + P_{EA} = 0 \qquad (5.1)$$

The external applied pressure will be considered to be equal to zero, resulting in a balance between the hydrostatic pressure and the various components of the disjoining pressure. These will be separately discussed in the next sections.

### 5.2.1 Hydrostatic pressure

For a vertical film as investigated in this study, the hydrostatic pressure is the pressure difference resulting from the gravitational field on a film of height l that is the difference between the point on the film considered and the surface of the bulk solution. The hydrostatic pressure is given by the relation:

$$P_H = -\Delta\rho g l \qquad (5.2)$$

where $\Delta\rho$ is the density difference between the liquid within the film and the surrounding medium, g is the acceleration due to gravity. The Plateau-border suction is also included in $P_H$.

### 5.2.2 Disjoining pressure

Various components of the disjoining pressure may be distinguished of which the attractive Van-der-Waals force and the repulsive force due to overlap of the electrical double layers are the most extensively discussed in the literature. A third component is steric interaction. This itself may be attractive or repulsive depending on the properties of the system. In the case of films formed from polymers or nonionic surfactants with a significant chain length this interaction force is very important and may dominate all other interactions.

In this study the Van-der-Waals forces and the electrical double layer repulsion are considered as known from theory. The hydrostatic pressure can be determined experimentally and hence at equilibrium the steric repulsion can be obtained using equation 5.1.

#### 5.2.2.1 *Van-der-Waals attraction*

Van-der-Waals attraction results mainly from the electromagnetic dispersion forces between the molecules of the film. Two different approaches have been used to obtain a relationship between the dispersion forces and the distance of separation between the surfaces. The first is based on the classical theory of London. In the so called "microscopic" theory (De Boer, 1936; Hamaker, 1937) the assumption is made that intermolecular dispersion forces are additive and that the total force between two bodies is obtained by integration over their total mass instead of summation of the forces between pairs of individual atoms. The second and mathematically more complex approach to the treatment of dispersion forces has been developed by Lifshits and coworkers (1955, 1959).

They considered the "macroscopic" effect of interaction of dielectric bodies. A detailed comparison of these two treatments has been given by Scheludko (1967).

Following the microscopic theory the attraction force between two flat semi-infinite parallel plates separated by a gap of thickness d (ignoring retardation effects) is given by:

$$P_A = \frac{-A_{11}}{6\pi d^3} \qquad (5.3)$$

where $A_{11}$ is the Hamaker constant of material 1 which is determined by:

$$A_{11} = \pi^2 q_1^2 \beta_{11} \qquad (5.4)$$

where $q_1$ is the number of atoms per $m^3$ and $\beta_{11}$ is the London dispersion constant for the interaction between two atoms of the same material and which is related to:

$$V_A = \frac{-\beta_{11}}{r_{11}^6} \qquad (5.5)$$

where $V_A$ is the London-Van-der-Waals attraction energy between two atoms at distance $r_{11}$ (calculated from the centres of the two atoms).

De Vries (1958) demonstrated that the compressive force on a liquid film is exactly equivalent to the force between two semi-infinite layers of solution separated by an air gap of the same thickness as the film, and can therefore be calculated using equation 5.3. Although there is still some difference in the results obtained by the microscopic and macroscopic theory due to the medium effect, additivity and relaxation (Scheludko, 1967), equation 5.3 can be used for liquid films without making too much errors.

Duyvis (1962) has shown that equation 5.3 is also valid in the case of a heterogeneous soap film, consisting of two identical hydrocarbon layers, each of thickness $d_1$, enclosing an aqueous

core of thickness $d_2$ under the condition that $d_2 >> d_1$ and a slightly different value for $A_{11}$. Anticipating the discussion of the structure of the liquid film of nonionics which will be given in section 5.3 it may be stated that application of equation 5.3 does not cause any serious error for two main reasons:

a. The segment concentration of the hydrophilic polymer part is low and all segments are strongly hydrated.
b. The contribution of the Van-der-Waals energy to the total interaction energy is relatively small.

To a good approximation the Hamaker constant can be taken as equal to that of water. The same assumption has been made previously for polymer films (Van Vliet, 1977) and for PVA-layers adsorbed on AgI (Fleer, 1971).

5.2.2.2 *Electrical double layer repulsion*

Although nonionic surfactants do not contain any intrinsic charge groups, there will still be a potential difference between the surface and bulk solution due to the preferential accumulation of ions of one charge type over the other charge at the surface. This will give rise to an electrostatic component, $P_E$, in the disjoining pressure. This component $P_E$ can be calculated using the DLVO theory. For two parallel plates at distance $d_2$ Verweij and Overbeek (1948) derived an approximate analytical expression for the repulsive force per unit area for symmetrical electrolytes:

$$P_E = 64 v_o k_B T \gamma_d^2 . \exp(-\kappa d_2) \qquad (5.6)$$

where $v_o$ is the number of counterions per unit volume and $d_2$ is the thickness between the two hydrocarbon layers. The reciprocal Debye lenght $\kappa$ and $\gamma_d$ are given by the following expressions:

$$\kappa = (2 v_o Z^2 e^2 / \varepsilon_d k_B T)^{\frac{1}{2}} \qquad (5.6a)$$

$$\gamma_d = \tanh(Ze\psi_d / 4 k_B T) \qquad (5.6b)$$

where Z is the valency of the counterion, e is the elementary charge, $\varepsilon_d$ is the dielectric constant of the medium and $\psi_d$ is the diffuse double layer potential. As in films stabilized by ethoxy-

lated surfactants there is no discrete transition between the polyoxyethylene part, charged by ion uptake, and the aqueous core; the notions $d_2$ and $\psi_d$ reflect a step function depicting the real gradual change of potential with distance. The condition $\kappa d_2 > 1$ on which equation 5.6 is based is satisfied in thin liquid films.

5.2.2.3 *Steric interaction*

Steric interaction results from the possible interaction of the adsorbed oligomers or polymer chains. In thin liquid films this steric interaction can be attractive or repulsive depending on the characteristics of the adsorbed polymer layer partly protruding in the aqueous layer. This interaction is basically due to a nonzero free energy of mixing. The increase of the segment concentration and the lowering of the conformational entropy upon overlap lead to repulsive interaction. One of the prerequisites for the understanding of steric interaction is therefore insight into the adsorption of macromolecules at an interface. This knowledge has seen a rapid development. Recent reviews about polymer adsorption have been published by Vincent and Whittington (1980) and Fleer and Lyklema (1983). The application of these modern polymer adsorption theories to steric stabilization is not yet fully elaborated (Scheutjens and Fleer, 1982, 1984). Besides, to date, most of the adsorption theories are restricted to homopolymers. A preliminary result of the Scheutjens-Fleer steric stabilization theory is that free liquid films can not be stabilized by pure homopolymers (Scheutjens, 1983). As far as the author is aware only copolymers have been used to stabilize free liquid films.

Heterodispersity of the polymer sample is another very important factor in steric interaction. Cohen Stuart *et al.* (1980) gave a quantitative analysis of this effect for homopolymers. They showed that fractionation at a surface occurs due to preferential adsorption of the high molecular weight fractions. Prediction of the adsorption of a heterodisperse copolymer is therefore difficult. It is obvious that in the case of an AB block copolymer with a strong amphiphilic character the effect of preferential adsorption of the high molecular weight fractions is less pronounced.

Considering the present lack of a complete theory, the steric interaction will only be described in a qualitative manner in this chapter.

## 5.3 Experimental

### 5.3.1 Light reflection

Optical properties of thin liquid films can be used for measuring the thickness of these films (Mysels *et al.*, 1959). When the film is transparant, homogeneous and isotropic, the ratio between the intensity of the incident light and reflected light is a measure for the thickness d of the film (Rayleigh 1902; Vašiček, 1960) (see also fig. 5.1):

$$R_i = \frac{I_r}{I_o} = \frac{4r^2 \sin^2\Delta}{1-2r^2 + 4r^2\sin^2\Delta + r^4} \qquad (5.7)$$

where $I_o$ and $I_r$ are the intensities of the incident and the reflected beam respectively, r is the Fresnel coefficient which will be defined below and $\Delta$ is the phase difference between the beams reflected at the frontside and the backside of the film. This $\Delta$ is related to the thickness d according to the following expression:

$$\Delta = \frac{2\pi n_f \cos\beta}{\lambda} \cdot d \qquad (5.8)$$

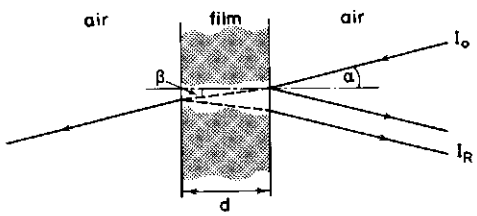


Fig. 5.1 Schematic representation of reflection of light by a homogeneous film

where $\lambda$ is the wavelength (in vacuum) of the light used, $n_f$ is the refractive index of the filmmaterial and $\beta$ is the angle of refraction which can be obtained using Snell's law:

$$\beta = \arcsin\left[(n_o/n_f)\cdot\sin\alpha\right] \tag{5.8a}$$

where $n_o$ is the refractive index of air and $\alpha$ the angle of incidence.

In the case of non-polarized light one has to take into account that light consists of two components. Therefore the Fresnel coefficient is a complex function (Vašiček, 1960):

$$r^2 = \tfrac{1}{2}\left[(r^s_{\alpha\beta})^2 + (r^p_{\alpha\beta})^2\right] = \tfrac{1}{2}\left[\frac{\sin^2(\alpha-\beta)}{\sin^2(\alpha+\beta)} + \frac{tg^2(\alpha-\beta)}{tg^2(\alpha+\beta)}\right] \tag{5.9}$$

For small angles ($\alpha<30^o$), equation 5.9 can, to a good approximation, be simplified to:

$$r^2 = \left[\frac{n_f-n_o}{n_f+n_o}\right]^2 \tag{5.9a}$$

For $n_f$=1.3325, $n_o$=1 and $\alpha=7.125^o$ the difference in the values between equations 5.9 and 5.9a is less than 0.04%. For this reason all calculations will be made using equation (5.9a). By measuring the ratio $I_r/I_o$ it is possible to calculate the value of sin $\Delta$ using equation 5.7. In practice the interference pattern $I_r(t)$,

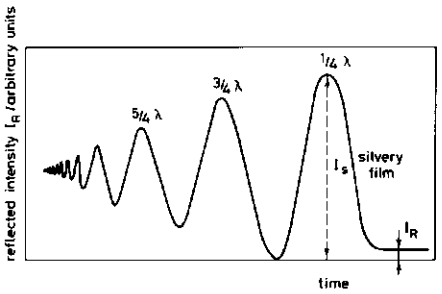


Fig. 5.2 Reflected intensity as a function of time

schematically represented in fig. 5.2 is used to obtain $I_r/I_o$. At maximum reflection (the last maximum is represented in fig. 5.2 by $I_s$), the phase difference ($\Delta$) is equal to $(\frac{1}{2}+k)\pi$, where k=0,1,2,3... and the film thickness is given by:

$$d_s = \frac{(1+2k)\lambda}{4n_f\cos\beta} \qquad (5.10)$$

where the subscript s refers to silvery film (denoted after its white appearance). Using the last silvery film as the reference and realising that $\sin^2\Delta=1$ for a silvery film, the following equation can be obtained (Bruil, 1970; Van Vliet, 1977):

$$\frac{I_r}{I_s} = \left[ \frac{1+2r^2+r^4}{1-2r^2+r^4+4r^2\sin^2\Delta} \right] \cdot \sin^2\Delta \qquad (5.11)$$

Substituting equation 5.8 in 5.11 and rearranging it follows that:

$$d = \frac{\lambda}{2\pi n_f\cos\beta} \arcsin \left[ \frac{(1-2r^2+r^4)\cdot(I_r/I_s)}{\{1+2r^2+r^4-4r^2\cdot(I_r/I_s)\}} \right]^{\frac{1}{2}} \qquad (5.12)$$

As the intensity of the last silvery film is used as standard, one must be certain that the measured last silvery film indeed represents the last maximum. This problem can be solved by using different wavelengths which should give the same film thickness. For films of sodium dodecylsulphates this has been shown by Bruil (1970). It is therefore justified to use the intensity of the last silvery film as standard.

The film thickness obtained with equation 5.12 is referred to as the *equivalent water thickness* ($d_{water}$). Equation 5.11 applies to a homogeneous film, which is not the case with surfactant films. For soap films a three layer sandwich-like structure has therefore been accepted (Clunie *et al.*, 1971) (see fig. 5.3a). An aqueous core with essentially bulk concentration is flanked by two surfactant monolayers. If there is a difference in refractive index between the different layers a correction has to be applied to $d_{water}$ to obtain the real thickness.

For polymer films a correction has also to be applied because the polymer segments are not homogeneously distributed. These films

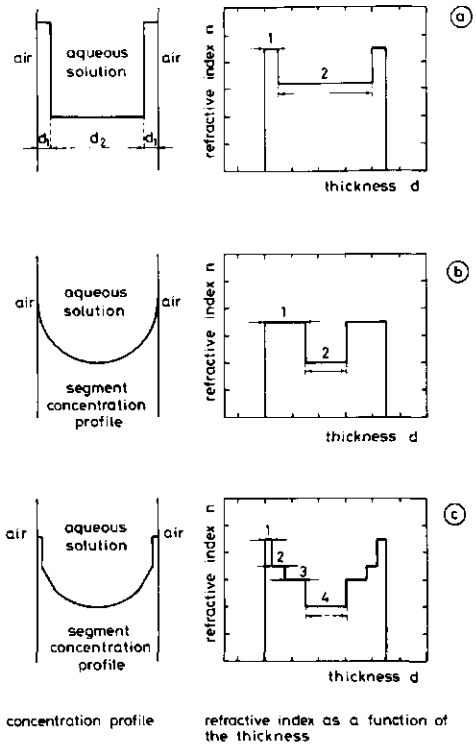


Fig. 5.3 Schematic model of a soap film a, polymer film b and a Synperonic NPE film c, used for the optical determination of the thickness

consist of two polymer monolayers which may or may not be separated by an aqueous core (Van Vliet, 1977)(fig. 5.3b).
For films stabilized by ethoxylated surfactants corrections for both the hydrophobic moiety and the ethoxy chain have to be applied (fig. 5.3c).

A correction for the difference in optical properties of the surface layers and the ensuing multiple reflections has been derived in a general way by Vašićek (1960) and by Frankel and Mysels (1966). This has been applied for soap films by Duyvis (1962) and by Lyklema *et al.* (1965) and for polymer films by Van Vliet (1977).

The theory of Frankel and Mysels (1966) can be used to obtain thickness corrections due to the inhomogeneous refractive indices in different layers in a simple way and will be used in this study. This theory neglects absorption and polarization effects and is therefore applicable only to normal or sufficiently near-normal incidence. These conditions have been met for the free liquid films studied in this work. Furthermore the assumption is made that the thickness of the interface layers is small compared to the wavelength of the reflected light. This assumption is justified since the film is considered as a collection of parallel sheaths, each with a thickness small compared to the wavelength of the light, and with a constant refractive index in each sheath. Frankel and Mysels (1966) obtained in this way the following expression:

$$\Delta d = (n_f^2-1)^{-1} \sum_{i=1}^{i=k_1} d_i \, (n_i^2-1) \qquad (5.13)$$

where $n_i$ is the refractive index of the $i^{th}$ layer with thickness $d_i$ and $k_1$ is the number of layers with a different refractive index. For the Synperonic films this equation can be applied by distinguishing between the nonylphenol part, the ethoxy chain and, in the case of NPE films, also the propylene oxide moiety. By analogy to the usual soap films the first layer is considered as pure nonylphenol, depicted in fig. 5.3c with thickness $d_1$ and refractive index $n_1$. For NPE films layer two in fig. 5.3c is the propylene oxide part with layer thickness $d_2$ and refractive index $n_2$ and layer three is the ethoxy chain with a layer thickness $d_3$ and refractive index $n_3$. Finally layer four is the aqueous solution. In the case of NP films there is no propylene oxide moiety present and hence the correction for layer two does not exist.

Van Vliet (1977) considered that polymer films consist of a collection of parallel sheaths of gradually changing index of refraction. By assuming that the refractive index decays exponentially with distance from the surface he could calculate a thickness correction. However, the difference between the correction using a multi step distribution and the one using a step function (like in soap films) was about ten per cent of the inaccuracy of the film thickness measurements. Therefore in our case a step function per layer

can be used for such a correction. As a result a five-layer-structure is adopted for the NP films and a seven-layer structure for the NPE-films, as depicted in fig. 5.3c.

For a seven layer structure equation 5.13 can be written as:

$$\Delta d_T = 2d_1 \cdot \left[\frac{n_f^2-n_1^2}{n_f^2-1}\right] + 2d_2 \cdot \left[\frac{n_f^2-n_2^2}{n_f^2-1}\right] + 2d_3 \cdot \left[\frac{n_f^2-n_3^2}{n_f^2-1}\right] = \Delta d_1+\Delta d_2+\Delta d_3 \qquad (5.13a)$$

where $\Delta d_T$ is the correction to be applied to the equivalent water thickness d of the film. The notions $d_1$, $d_2$ and $d_3$ are the thicknesses of the first, second and third layer respectively as depicted in fig. 5.3c with the corresponding refractive indices $n_1$, $n_2$ and $n_3$ respectively. For a five-layer structure the second term on the RHS of equation 5.13a is of course equal to zero.

Although in this model the liquid film is divided in several separate sheaths it is obvious that in reality the changes between the different sheaths are gradual rather than abrupt.

Recently Leermakers *et al.* (1983) showed by a statistical thermodynamical theory for the formation and description of amphiphilic bilayer membranes that the membrane properties are subject to considerable fluctuations. They showed that the thickness of a bilayer is not a statical but a statistical quantity. This corresponds with the experimental esr-spin labeling results of Povich *et al.* (1971). The latter authors showed that the surfactant molecule is not grossly immobilized by its incorporation into a soap film. Moreover the former authors showed that there is always a nonzero amount of solvent present in the hydrophobic part of the bilayer. The presence of this water must be taken into account in the calculation of the refractive index of the different sheaths. Direct evidence for the presence of water in the hydrocarbon layer was obtained from the refractive index measurements of the various layers of a free liquid film by Corkill *et al.* (1965). From reflection and Brewster angle measurements of a thin soap film they concluded that the surface refractive indices of the hydrocarbon layers were significantly less than those for the corresponding pure liquids. From their results a fraction of 30% water in the hydrocarbon layer can be calculated. From permeability studies of

soap films to gases Princen *et al.* (1967) had also to conclude that the hydrocarbon layers must contain some water. The differences between the values of the water contents in the hydrocarbon core obtained by Leermakers *et al.* (1983) and Corkill *et al.* (1965) may be due to the different films studied. The latter authors measured experimentally free liquid films, whereas the formers calculated the water content from theoretical considerations.

In this study the values of the refractive indices for free liquid films obtained by Corkill *et al.* (1965) were used.

### 5.3.2 Apparatus

#### 5.3.2.1 *Mechanical part*

The mechanical part of the apparatus used for the film thickness measurements was a modified form of the one described by Bruil (1970). The cell (fig. 5.4) was constructed by J.L.C. Verhagen (Laboratory for Physical and Colloid Chemistry, Agricultural University, Wageningen, The Netherlands). The vertical films were formed in glass frames with a width of 0.0125 m and a height of 0.015 m. The frame was initially immersed in a glass container filled to the top with surfactant solution. The container and the frame were placed in a water-thermostatted brass cell. The temperature was controlled within 0.01 K. In the front wall of the brass cell double glass windows were mounted. This cell was placed in a perspex cylinder and the whole apparatues was placed on an optical bench, built by H.E. van Beek (Laboratory for Physical and Colloid Chemistry). The optical bench itself was placed on four dampers (each with a different resonance time) to eliminate vibrations which could interfere with the measurements. The bench was enclosed in an air-thermostatted cabinet. The temperature of this cabinet was slightly higher than that of the brass cell in order to prevent condensation on the glass windows of the box. The inside of the cell was painted black to prevent stray light. The glass frame was attached to a perspex rod which could be connected to a screw micrometer (fig. 5.4). The spindle of this micrometer was attached to a stepper motor mounted vibration free by a flexible connection. The motor itself was not placed on the optical bench. The motor was controlled by a microprocessor (Eurocom 1)

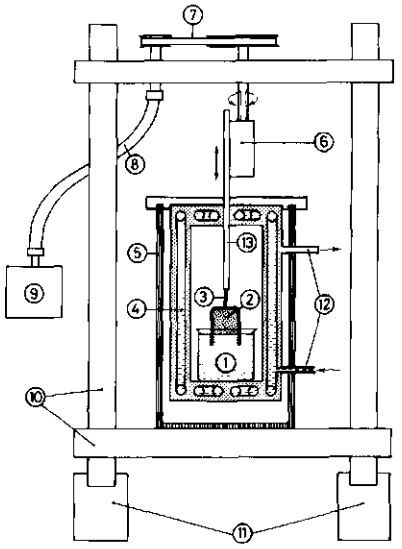


Fig. 5.4 Schematic representation of the apparatus for measuring the thickness of free liquid films. Mechanical part

1 glass container with surfactant solution
2 film
3 glass frame
4 water thermostatted brass box
5 perspex box
6 adjustment device for raising or lowering the glass frame, with known pitch
7 driving belt
8 vibration free flexible connection
9 stepper motor
10 support (part of the optical bench)
11 vibration damper
12 inlet and outlet for thermostatting water
13 perspex rod

in such way that a large range of constant pulling velocities (0.1 $\mu ms^{-1}$ - 2000 $\mu ms^{-1}$) of the frame could be achieved. This

microprocessor also controlled several other functions making fully automatised measurements possible under well-defined conditions.

5.3.2.2 *Optical and electronic part*

The light source was a Spectra Physics (model 155) 0.5 mW helium-neon laser with a characteristic wavelength of 632.8 nm. A schematic representation of the optical and electronic setup is given in fig. 5.5 as well as the data transmission and control lines from the microprocessor. The laser beam was directed horizontally at an angle of 7° to the vertical film via an attenuation (16 times) a chopper and a mirror.

The light spot, in the middle of the film, had a diameter of $10^{-3}$m and was situated $6 \cdot 10^{-3}$ m above the meniscus of the bulk solution. The reflected beam from the film was directed to a photodetector (A) (Hewlett Packard-PIN photodiode 5082-4204). In order to eliminate fluctuations in laser intensity, use was made of a reference beam: light reflected by one of the glass windows was directed onto a second (identical) photodetector (B). Interference from

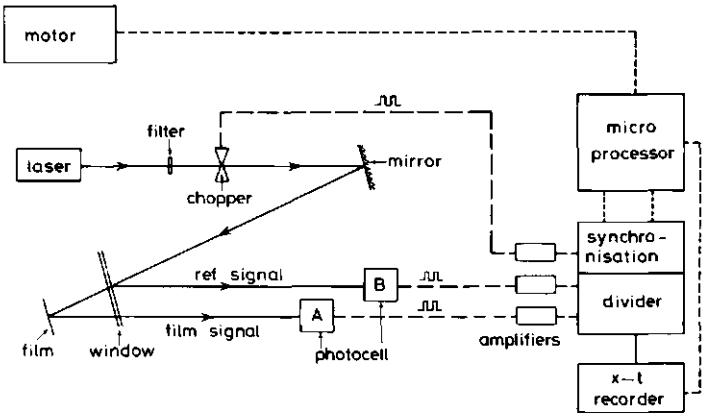


Fig. 5.5 Schematic representation of the apparatus for the measurement of the thickness of free liquid films. Optical and electronic part.

stray light was eliminated by modulating the laser beam by means of a chopper (180 Hz) and amplifying the signals of the photodiodes with a synchronous amplifier, which only amplifies signals having the chopper frequency and phase. The amplification of the film reflection signal and the reference singal were independent of each other. The two alternating current signals were transformed into direct current signals, which could be amplified in such a way that they were of the same order of magnitude. Subsequently the film signal was divided by the reference beam signal and the current coming from the divider (Intech A733) was registered by a Philips type PM8202 recorder. An autoscaling mechanism built in the electronic device provided optimum accuracy. The complete electronic system was designed and built by R.A.J. Wegh (Laboratory for Physical and Colloid Chemistry).

### 5.3.3 Measurements and calculations

#### 5.3.3.1 *Measurements*

Prior to each set of measurements with a given surfactant solution, the glass container and the glass frame were cleaned by immersing them in chromic acid for at least 12 hours to remove surface active components. After rinsing several times with tap-water and deionised water (Millipore MilliRO60 filter combined with a Super Q system, specific conductivity below $10^{-4}$ $\Omega m^{-1}$) the container and frame were dried at 383 K.

Surfactant solutions were filtered through a membrane filter (pore size $0.25 \cdot 10^{-6}$ m) under nitrogen pressure. Prior to the measurement the solution was filtered a second time through a G2 glass filter directly into the glass container. To avoid any dust this was done in an anti-dust cabinet (Slee, London). After the container was filled to the top with surfactant solution and after the glass frame had been immersed, the cell was closed tightly and mounted on the optical bench. Immediately thereafter some films were drawn in order to promote equilibration between the solution and the atmosphere within the cell. After about ten hours reliable measurements could be performed.

As mentioned before the measurements were controlled by a microprocessor. A programme was written by M.Vos (Laboratory for Physic-

al and Colloid Chemistry). Every minute the signal from the photodetector A was checked. When after five consecutive readings no signal from the film was measured, the film was taken to have collapsed, the frame was immersed in the surfactant solution again and pulled out after a preset time. The observation time of a given film could also be varied, after which the frame was immersed and pulled out again to make a new film. In this way more measurements could be performed, and they could be measured under better defined conditions than manually. The average thickness of ten or more films from one solution was taken as the film thickness.

5.3.3.2 *Calculations*

The ratio between the intensity of the final film and the intensity of the last silvery film was obtained from the recorder paper. The equivalent water film thicknesses were first calculated using equation 5.12, where $\lambda=632.8\cdot10^{-9}$m and $\alpha=7.125°$. For the Fresnel coefficient equation 5.9a was used where $n_o$ was taken as unity and $n_f$ depended on the concentration of the surfactant and the electrolyte. All values for $n_f$ were based on measurements of the refractive index at the sodium D line ($\approx589.3\cdot10^{-9}$m). The difference between the refractive index at the wavelength of the He-Ne laser and at the Na-D line is less than 0.1% for optical glass. For thin films this would lead to a maximum error of less than 0.1% and the corresponding error of the film thickness would be much smaller than 0.1%. Therefore this was neglected in the calculations. Differences in refractive index due to temperature variations were also neglected. According to the data of the Critical Tables the difference between the refractive index at 288 K and at 308 K is less than 0.2% which would result in an even smaller error in the film thickness.

At not too high concentrations the refractive index of a mixture can be calculated with equation 5.14 according to Cain *et al.* (1978) and Liang and Fitch (1982):

$$n_f = n_{water} + [(dn/dc)\cdot c]_{pol} + [(dn/dc)\cdot c]_{elect} \qquad (5.14)$$

The refractive index increments used for this calculation are given in table 5.1. The value for Synperonic NPE was experimental-

ly determined and agreed very well with the value for PEO (Brandrup and Immergut, 1975). The values for the electrolyte solutions were taken from the literature (Weast, 1978).

In order to apply the theory of Frankel and Mysels (1966) appropriate values for the thickness of the replaced layer and its refractive index must be known.

A realistic model for the film structure of NPE surfactants is a seven-layer model (see section 5.3.1). To estimate the refractive index of the first layer ($n_1$) the refractive index of pure nonylphenol should be known. This can be measured or estimated from literature data. The indices of refraction of pure homogeneous ethoxylated octylphenols have been measured by Mansfield and Locke (1964) as a function of the number of ethoxy groups. These values can be extrapolated to yield the refractive index of octylphenol itself. This gives a value of 1.517. The latter value agrees well with the measured value (1.513) of nonylphenol which was obtained using an Abbe refractometer ( Atago model 301). Taking into account the results of Corkill *et al.* (1965) a value of $n_1$=1.46 can be calculated for the refractive index of the first layer. This result agrees very well with the value of 1.45 used by Bruil (1970) for OP 11.

Table 5.1 Refractive index increments.

| Species | dn/dc ($m^3 kg^{-1} \cdot 10^{-4}$) |
|---|---|
| NPE | 1.4 |
| $Na_2SO_4$ | 19.9 |
| NaCl | 8.9 |
| NaBr | 13.2 |

The thickness of the nonylphenol layer can be obtained from the results of Leermakers *et al.* (1983). These authors showed that the thickness of a bilayer is about 40 per cent of the corresponding extended chains. This means that, on average, $d_1$ is roughly 0.4 times a fully extended hydrocarbon chain. This gives a thick-

ness of $d_1=0.68\cdot10^{-9}$m. Alternatively the method of Lyklema *et al.* (1965) can be applied, by which the molecular area has been used to calculate $d_1$. The molecular area for the nonylphenol was estimated from an extrapolation of the data of Hsiao *et al.* (1956), and assuming a density of 1. This gives a value of $d_1=0.65\cdot10^{-9}$m. Both results agree very well with each other leading to a correction of $\Delta d_1=0.6\cdot10^{-9}$m.

A correction for the different optical properties of the propylene oxide layer was made following the methode of Van Vliet (1979). All the polymer is considered to be present in one layer. The maximum volume fraction of the polymer is 0.7 and the rest is water in conformity with the results of Corkill *et al.* (1965). The refractive index $n_2$ of the second layer can be calculated from a knowledge of the refractive index of PPO. This latter can be obtained from refractive index values of PPO in some organic solvents (Brandrup and Immergut, 1975) and taking a value of 1200 kg $m^{-3}$ for the density. This gives a value of 1.46 for the refractive index of PPO at 298 K which compares well with similar polymers. For a mixture of poly(propylene oxide) and water a value of 1.42 for the refractive index was used.

The thickness $d_2$ of the second layer was calculated form the molecular areas of Hsiao *et al.* (1956), using equation 5.13 for $\Delta d_2$. The results are included in table 5.2.

A third correction has to be applied for the PEO-layer. Again considering the PEO as a separate sheath containing water with a volume fraction of 0.3, the refractive index ($n_3$) and the thickness ($d_3$) can be calculated. The results are also included in table 5.2.

A correction for a five-layer model (Synperonic NP surfactants) can be easily obtained by taking $\Delta d_2=0$.

The values given in table 5.2 tend to exceed those normally found in literature, because of more appropriate values for the indices of refraction and a more realistic film composition.

Table 5.2 Thickness of the various sheaths and calculated correction factors

| Surfactant | $d_1$ (nm) | $\Delta d_1$ (nm) | $d_2$ (nm) | $\Delta d_2$ (nm) | $d_3$ (nm) | $\Delta d_3$ (nm) | $\Delta d_T$ (nm) |
|---|---|---|---|---|---|---|---|
| NP 10 | 0.65 | -0.6 | | | 1.53 | -0.78 | -1.38 |
| NP 15 | 0.65 | -0.6 | | | 1.91 | -0.98 | -1.58 |
| NP 20 | 0.65 | -0.6 | | | 2.23 | -1.14 | -1.74 |
| NPE 1800 | 0.65 | -0.6 | 1.68 | -0.94 | 2.56 | -1.31 | -2.85 |
| NPE A | 0.65 | -0.6 | 1.24 | -0.69 | 3.63 | -1.86 | -3.15 |
| NPE B | 0.65 | -0.6 | 0.97 | -0.54 | 4.81 | -2.46 | -3.60 |
| NPE C | 0.65 | -0.6 | 0.67 | -0.37 | 7.27 | -3.73 | -4.70 |

## 5.4 Results and discussion

In this section the results of the equilibrium film thickness measurements will be given and discussed. These results will be compared with other film thickness results taken from literature. It will be shown that the results can be described in terms of a simple model involving an effective hydrodynamic volume for the surfactant molecules.

### 5.4.1 Drainage behaviour

Depending on their drainage behaviour free liquid films may be classified into two main categories: *rigid* and *mobile*. The difference between the two types of films is a high surface shear viscosity for the rigid one, that is absent in mobile films. This can be demonstrated in vertical frames where mobile films thin in a matter of minutes with a regualr filmprofile, whereas rigid films take hours or days to drain completely giving an irregular filmprofile. No sharp distinction between the two types of films can be made.

The drainage times of films stabilized by Synperonic NP or NPE surfactants in the present study varied between 0.5 and 2 hours depending on the type of surfactant and on the nature and concentration of electrolyte used. A film of Synperonic NPE 1800 drained

in about 1.5 hours. In the presence of a high concentration of electrolyte (0.4 M $Na_2SO_4$ or 4 M NaCl) this time was reduced to 0.5 hours. From the drainage time and the regular film profile (shown by the continuous reflectance pattern) it was concluded that all films studied belonged to the mobile category.

### 5.4.2 Equilibrium film thickness

The results of equilibrium film thickness measurements as a function of the Synperonic NPE 1800 concentration are shown in fig. 5.6. A similar behaviour was found for Synperonic NPE C (not shown). As can be seen, the thickness is independent of the concentration. The lowest concentration that produces stable films is more than ten times the c.m.c. At the c.m.c. itself only one stable film, from about a hunderd trials, with a thickness of 47 nm was obtained (this result is not included in fig. 5.6). This is qualitatively in agreement with the work of Paluch (1980), who measured the film thickness of OP 9 (also an ethoxylated nonionic surfactant) as a function of the surfactant concentration at nearly the same hydrostatic pressure and found a constant thickness at concentrations several times the c.m.c. However by lowering the concentration the thickness increased till unstable films were formed. Bruil

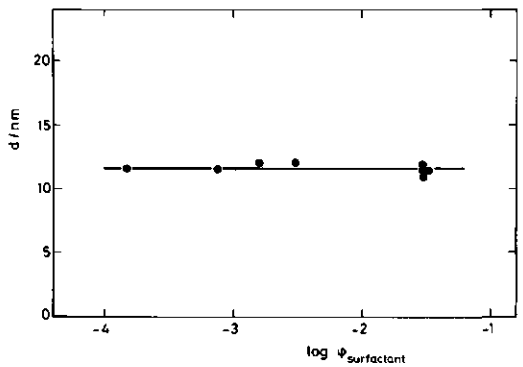


Fig. 5.6 Thickness of equilibrium films stabilized by Synperonic NPE 1800 as a function of surfactant concentration at 298 K

(1970) also found a constant thickness for OP 11 stabilized films for concentrations above the c.m.c.

Since the film thickness is determined by the interaction forces exerted by the adsorbed surfactant molecules, these results may be explained in terms of the adsorption behaviour of the Synperonic molecules. As was shown by Cohen Stuart *et al.* (1980) heterodispersity of homopolymers affects their adsorption behaviour. The amount adsorbed increases with increasing chain lenghts, long molecules adsorbing preferentially over shorter ones; this also affects the layer thickness. Therefore with a polydisperse system fractionation occurs, the short molecules preferentially enriching the solution and the long chains preferentially adsorbing on the surface. This effect is more pronounced at a low surface-area-to-volume ratio (A/V) such as in liquid films (Fleer and Lyklema, 1983). This followed also from the experiments by Lyklema and Van Vliet (1978) for the heterodisperse copolymer PVA: by increasing the polymer concentration at a constant hydrostatic pressure the film thickness increased.

However for heterodisperse nonionic surfactants the above effect is not so simple, since heterodispersity may involve variation of the hydrophobic-hydrophilic balance. At a given hydrophobic chain length a longer hydrophilic tail reduces the tendency for adsorption. Although the Synperonic surfactants are heterodisperse regarding the ethoxy chain (chapter 2) the film thickness is constant over the concentration range studied. This may account for the fact that the lowest concentration of the surfactant studied is already too high for showing the fractionation effect. In addition thinner films would be expected at lower c.m.c. which is opposite to the results of Paluch (1980). The consequences of heterodispersity for liquid films will be discussed in more detail in section 5.4.2.2.

From the above results it can be concluded that the independence of film thickness on the concentration suggests that the repulsive forces exerted by the adsorbed molecules are also constant.

In the following sections we will discuss the influence of the hydrophilic chain length, addition of electrolytes, temperature and the composition of mixtures with different chain lengths.

5.4.2.1 *Influence of ethoxy chain length*

The equilibrium thicknesses of films stabilized by Synperonic NP and NPE with varying ethoxy chain lengths are given in table 5.3. The concentration was sufficiently above the c.m.c. to obtain equilibrium films. The equivalent water thickness and the real thicknesses are both given to allow comparison with literature

Table 5.3 Equilibrium thickness data of the Synperonic NP and NPE surfactants obtained with the free liquid film technique. No electrolyte added.

| Surfactant | $n_{EO}$ | equivalent water thickness (nm) | film thickness (nm) |
|---|---|---|---|
| NP 10 | 10 | 9.5 | 8.1 |
| NP 15 | 15 | 10.3 | 8.8 |
| NP 20 | 20 | 11.3 | 9.5 |
| NPE 1800 | 26 | 14.4 | 11.6 |
| NPE A | 50 | 17.0 | 13.9 |
| NPE B | 85 | 19.3 | 15.7 |
| NPE C | 190 | 27.8 | 23.1 |

values. The value of Synperonic NP 10 is in good agreement with results obtained with octylphenol ethylene oxide surfactants (OP). For example with nearly the same ethoxy length Bruil (1970) obtained a thickness of 9.6 nm for OP 11 and Paluch (1980) found a thickness of 8.0 nm for OP 9. The small difference between the latter values and those obtained with Synperonic NP 10 are probably due to the difference in nature, extent of branching and some other unknown variables.

The thickness of an adsorbed layer can be measured using a wide range of methods (Tadros, 1982). Since various techniques can lead to different effective thicknesses, it is essential to compare results of these various techniques. A useful comparison of the layer thickness of PVA on PS-latex has already been given by Garvey *et al.* (1976). The latter authors used methods of diffusion

(from inelastic light scattering), rates of sedimentation (in the ultracentrifuge), electrophoretic mobilities and sediment volumes to obtain the thicknesses of adsorbed PVA on PS latex. Lyklema and Van Vliet (1978) have also compared the ellipsometric layer thicknesses of adsorbed PVA with the free liquid film thickness stabilized by this polymer.

Cohen Stuart *et al.* (1984) demonstrated that streaming potential measurements can also be used to measure the thickness of an adsorbed layer. They showed, however, that the electrokinetically determined layer thicknesses depend on the ionic strength. In the absence of electrolytes this thickness should be at its maximum and should be equal to the real (hydrodynamic) thickness. However, the latter value can only be obtained by extrapolation. This procedure has been applied to Synperonic NPE surfactants adsorbed at hydrophobised glass. The limiting value obtained in this way is compared with half the thickness of the free liquid film in table 5.4. The results obtained for the different surfactants agree very well, indicating that both techniques are consistent and hence reliable. Moreover, this agreement strongly supports the correctness of the applied optical correction of the liquid film thickness (section 5.3.3.2).

Table 5.4 Comparison of layer thickness

| Surfactant | hydrodynamic thickness (nm) | half the film thickness (nm) |
|---|---|---|
| NPE 1800 | 5.8 | 5.8 |
| NPE A | 6.4 | 6.9 |
| NPE B | 8.5 | 7.9 |
| NPE C | 11.5 | 11.6 |

The increase in filmthickness with increasing number of the ethoxy units of the NP and NPE type surfactants is obvious. The difference in film thickness stems from the difference in the repulsive contribution of the disjoining pressure orginating from the overlap of chains adsorbed on opposing surfaces. To quantify this repulsive interaction a very simple model will be adopted. The nonylphenol

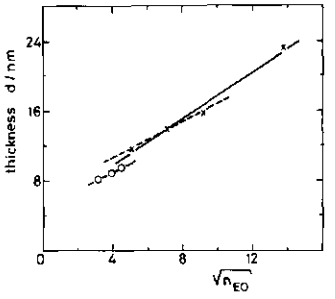


Fig. 5.7 Dependence of the equilibrium thickness of free liquid films stabilized by Synperonic surfactants on the number of ethylene oxide units at 298 K.
x = Synperonic NPE and o = Synperonic NP

(and for the Synperonic NPE also the PPO) parts of the molecule are considered to be strongly adsorbed. As a consequence the PEO chain is thought to behave as a terminally anchored tail, which may assume dimensions not much different from those for a free coil of the same ethoxy length. Therefore a square root dependence of the film thickness on the number of ethoxy units is appropriate:

$$d = I_{ft} + S_{ft} \sqrt{n_{EO}} \qquad (5.15)$$

In fig. 5.7 this relationship is graphically shown to apply for the Synperonic NP and NPE surfactants. The value of $I_{ft}$ corresponds to the thickness contribution of the anchoring moiety and the value of $S_{ft}$ depends on the solvent quality. Using this model and the results obtained for the Synperonic NP and NPE surfactants, the thickness contributions of the various sheaths (section 5.3.3.2) can be calculated and compared with the results included in table 5.2.

At fixed ethoxy chain length, the difference in film thickness between the Synperonic NP and NPE type surfactants can be attributed to the presence of the propylene oxide moiety in the NPE-series. This difference should be reflected in the value of $I_{ft}$

for both types of surfactants. However an extrapolation using equation 5.15 for all four Synperonic NPE's yields a smaller value for $I_{ft}$ (NPE) than the extrapolated value for the three Synperonic NP's. Moreover the values of $S_{ft}$ for the two types of surfactant deviate considerably. This deviation may be due to the limitation of the extrapolation procedure, which is determined by the maximum tail length that is allowed. For example, if the extrapolation is made without the film thickness of NPE C, the value of $S_{ft}$ for Synperonic NPE is nearly the same as that for Synperonic NP as should be expected. A reasonable explanation could be that with relatively large tail lengths the model used is not appropriate. For example, for relatively short tails the swelling due to the excluded volume effect is probably negligible, whereas for rather long tails this is not the case. Since the Synperonic NP surfactants have relatively short ethoxy tails, it may be justified to use only the Synperonic NPE surfactants with a not too large tail length in the extrapolation procedure. This gives a value of $d_2$= 0.9 nm (fig. 5.3c) independent of the length of the ethoxy moiety.

Extrapolating of the film thickness of Synperonic NP according to equation 5.15 yields for the thickness of the nonylphenol layer $d_1$=2.3 nm.

For the surfactants used in this study, theoretical treatments assuming permanently anchored chains are appropriate (Levine *et al.* 1978) and these invariably show large repulsive forces already at slight overlap of the adsorbed layers. Therefore in the proposed model the film thickness due to the ethoxy chain of the surfactants will be equal to the sum of the diameters of two random coils touching each other just in the middle of the film. The diameter of a random coil can be related to its hydrodynamic volume which, in turn, is related to the intrinsic viscosity by (Tanford, 1961 p. 391):

$$V_h = \frac{[\eta] \cdot M_{EO}}{2.5 \cdot N_{Av}} \qquad (5.16)$$

Table 5.5 Effect of lateral compression on the cross sectional area and on the layer thickness

| Surfactant | $d_{EH}$ (nm) | $d_{EO}$ (nm) | $\sigma_{EH}$ ($nm^2$) | $\sigma_{EO}$ ($nm^2$) | $d_{EO}/d_{EH}$ | $(\sigma_{EH}/\sigma_{EO})^{1/3}$ |
|---|---|---|---|---|---|---|
| NP 10 | 2.2 | 3.4 | 0.94 | 0.60 | 1.55 | 1.16 |
| NP 15 | 2.7 | 4.1 | 1.42 | 0.72 | 1.52 | 1.25 |
| NP 20 | 3.2 | 4.8 | 1.97 | 0.82 | 1.50 | 1.34 |
| NPE 1800 | 3.7 | 4.9 | 2.67 | 1.15 | 1.32 | 1.32 |
| NPE A | 5.4 | 7.2 | 5.73 | 1.18 | 1.33 | 1.69 |
| NPE B | 7.4 | 9.0 | 10.65 | 2.22 | 1.22 | 1.69 |
| NPE C | 11.6 | 16.4 | 26.39 | 2.99 | 1.41 | 2.05 |

where $M_{EO}$ is the molecular mass of the polyoxyethylene chain and the other symbols have their usual meaning. The molecular mass can be calculated from the MKS-equation (section 3.7). The empiricial expression of Molyneux (1975) may be used (equation 3.32a), although this equation is only valid if $M > 0.7$ kg $mol^{-1}$. For lower values of M equation 3.32b should be used instead (Molyneux, 1975):

$$[\eta] = 11.25 \cdot 10^{-5} M_v^{0.5} \qquad (3.32b)$$

The results obtained for the effective hydrodynamic thickness ($d_{EH}$) are given in the first column of table 5.5. As can be seen, these values are lower than the experimentally obtained values which are shown in the second column of table 5.5. These experimental values have been obtained by subtracting $l_{ft}$ from the film thickness. However the values calculated in this way correspond to a free coil with no interaction of neighbouring coils. As the concentration of coils next to the interface is too high for such an ideal behaviour a correction has to be applied. The situation is analogous to that of a random coil trapped in a narrow tube, which has been treated by De Gennes (1979). The latter author derived an equation for the elongation of such trapped coils as a function of the diameter of the tube:

$$R_{11} \sim D_c^{-2/3} \qquad (5.17)$$

where $R_{11}$ is the length of the deformed coil parallel to the axis of the cylinder and $D_c$ is the diameter of the cylinder. If this dependence applies to our system, the following relation should hold:

$$\frac{d_{EO}}{d_{EH}} = \left(\frac{\sigma_{EH}}{\sigma_{EO}}\right)^{1/3} \qquad (5.18)$$

In this equation $\sigma_{EO}$ is the area per molecule which can be obtained from surface tension measurements. For Synperonic NPE the data of table 3.1 are taken and for the Synperonic NP the values of Hsiao *et al.* (1956). All the results are also collected in table 5.5 which shows good agreement between the two ratios indicating that elongation of the surfactant molecules is likely to be caused by lateral compression which influences the film thickness.

5.4.2.2 *Influence of heterodispersity.*

As indicated previously the film thickness is independent of the surfactant concentration. This suggests that heterodispersity does not influence the film thickness, because no fractionation occurs i.e. all molecules have the same adsorption energy. To verify this suggestion film thicknesses of mixtures of Synperonic NPE 1800 and NPE C were measured. If heterodispersity plays a role, this would be reflected in the film thickness in the following way. Suppose small molecules would adsorb preferentially, then upon enriching the mixture with the high molecular mass compound, the film thickness would keep the same low value until a certain mixture composition is reached. Upon further enriching the mixture with the high molecular mass compound the thickness would increase rapidly until the thickness is attained corresponding to the long species alone. The reverse feature would be observed if the high molecular mass fractions would adsorb preferentially. However, if there is no preferential adsorption of one of the species, there will be a gradual increase in thickness as a function of the mixture composition, because then the bulk and the surface compositions are identical. This will lead to some space for the large

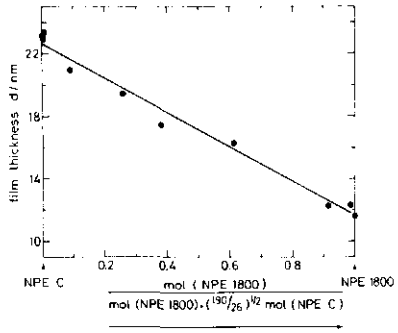


Fig. 5.8 Film thickness as a function of composition in a mixture of Synperonic NPE 1800 and NPE C at 298 K

molecules in lateral direction. This space will diminish proportionally with the composition of the mixture.

In fig. 5.8 the film thickness is shown as a function of composition of Synperonic NPE 1800 and NPE C. On the abscissa axis the composition of the mixture is represented by a kind of mole fraction in which the dependence of the film thicknesses on the square root of the number of ethylene oxide groups is taken into account. Because the optical correction factors for Synperonic NPE 1800 and NPE C are not equal (table 5.2) a linear interpolation of these factors is applied for the mixtures. As can be seen from fig. 5.8 a linear dependence of the film thickness on this mole fraction is obtained, over the entire range.

It is concluded that fractionation of a polydisperse sample at the air-water surface does not occur.

### 5.4.2.3 *Influence of nature and concentration of electrolytes*

As will be shown in the next chapter, addition of electrolytes can influence the stability of dispersions and emulsions stabilized by Synperonic surfactants. The adsorption and flocculation were discussed in chapter 4. The addition of electrolytes affected both flocculation and coalescence although the effect was not large for the coalescence process.

As the stability of emulsions is dependent on the stability of the liquid film formed upon approach between two emulsion droplets, it is worthwhile to study the corresponding features in thin liquid films with particular reference to the influence of electrolytes upon the thickness of these liquid films. However some remarks should be made in advance. Firstly there are some experimental limitations. As has been shown in chapter 4 flocculation only occurs on addition of electrolytes, at temperatures above 298 K. However film thickness measurements at these temperatures appeared to be impossible because of technical difficulties (see next section). Consequently it was decided to study the film thickness as a function of electrolyte addition only at 298 K. Therefore the thicknesses were measured under conditions where flocculation of the dispersion does not occur.
Secondly, coalescence occurs upon addition of electrolytes as the thin film formed between the *paraffin oil* droplets breaks, whereas in free liquid films the apolar phase will be *air*.
Therefore the results obtained with the free liquid films as a function of electrolyte concentration can not be applied directly to the emulsions, although the obtained general trend might help in understanding emulsion coalescence.

Electrolytes affect the thickness of liquid films in various ways. In the first place they can reduce the solvent quality and this will have several consequences. The adsorption of surfactant molecules will be promoted (table 3.2) resulting in a reduction of the molecular cross section of the surfactant molecule. Assuming that no desorption will occur this will increase the lateral compression and resulting in an increase in the elongation of the ethoxy chain according to equation 5.18. However, due to the lowering of the solvent quality the excluded volume effect will decrease. This effect will cause shrinking of the expanded coil which, in turn, will affect the diameter (perpendicular to the interface). As a result of the latter effect the film becomes thinner. Moreover, the reduction in excluded volume effect will decrease the elongation caused by the lateral compression. Perhaps there are still other influences. At any rate, both an increase and a reduction of the film thickness are possible consequences of electrolyte addition.

The reduction of the solvent quality depends on the type of electrolyte (chapter 4). Napper (1970b) interpreted this in terms of the triple region model for aqueous electrolyte solutions proposed by Frank and Wen (1957). In this model it is assumed that a layer of ordered water exists around an ion. This ordered layer, named region A, is oriented by the electrostatic field of the ion and forms part of the hydrodynamic unit. The normal water structure is destroyed in this layer. This A region is surrounded by a second region. In this B region the water molecules are less ordered compared with those in the A region and pure water. At large distances outside the intermediate B zone, the normal water structure, region C begins. The boundary between the two regions B and C is not sharp and one or more of the three types of regions may be absent. According to Napper (1970b) only the B and C region are accessible to PEO-chains. Based on this model Napper (1970b) postulated that ions with an extensive A region do not interact with PEO, however ions with no A region but with a large B region interact strongly with the polymer. Therefore the film thickness will also depend on the type of ions added.

The film thickness also depends on the length of the ethoxy chain, because swelling due to the excluded volume will be small or even negligible in the case of short chains. Therefore the reverse (= the diminishing of the elongation) will also be less for short tails.

Since both effects, increase of adsorption and reduction of the elongation will occur simultaneously it will not be easy to predict how the film thickness will change as a function of electrolyte concentration and it must be anticipated that in some cases the thickness exhibits an extremum as a function of electrolyte concentration.

Another possibility of interaction of electrolytes is ion absorption, which has been shown to occur by Buscall *et al.* (1975, 1976). Through electrostatic repulsion the layers will repel each other. The distance from the surface, within the adsorbed surfactant layer where ion absorption occurs, determines the extent of separation of the layers.

If ion absorption plays a role in the thickness of free liquid films stabilized by nonionic surfactants, it would be difficult to predict the trend of the film thickness as a function of the electrolyte concentration, but some general trends may be expected. For example if ion absorption occurs only at high concentration of electrolytes in the bulk, then the electrostatic repulsion could be much reduced due to the compression of the electrical double layers by the bulk electrolytes (equation 5.6). Under these conditions the film thickness will be unaffected by electrolytes. However if ion absorption occurs at low electrolyte concentrations, repulsion will ensue before the compression of the electrical double layer is complete. In that case, an increase in film thickness can be expected on initial addition of electrolytes followed by a decrease to the original thickness at high electrolyte concentration. Therefore if ion absorption occurs, a reduction in film thickness below the original value will never be obtained. These phenomena will also depend on the valence of the added electrolytes. Of course there is no sharp distinction between these actions and they can probably occur simultaneously.

The experimental results are given in fig. 5.9, where the abscissa axis represents the ionic strength to facilitate comparison of the different electrolytes. It is clear from this figure that for the monovalent electrolytes the film thickness passes through a maximum, but never reaches a value below the original film thickness at the electrolyte concentrations studied. For $Na_2SO_4$ a similar pattern was found with only one exception: a small increase in film thickness at the highest concentration studied.

As mentioned above comparison with other results of liquid film measurements after addition of electrolytes is difficult, due to the different types of surfactants used. Only Clunie *et al.* (1970) and Buscall *et al.* (1975, 1976) measured the effect of addition of electrolytes on film thickness stabilized by DMS, a different surfactant as has been used in the present study. These authors found that the film thickness was independent of a sodium chloride concentration up to a certain critical value above which there was a sharp increase in the film thickness with further increase in NaCl concentration. When the electrolyte concentration was

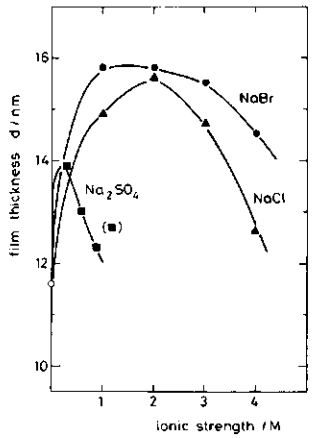


Fig. 5.9 Influence of nature and concentration of electrolytes on the thickness of free liquid films stabilized by Synperonic NPE 1800 at 298 K.

further increased the film thickness was found to decrease gradually; eventually it reached the initial equilibrium thickness in the absence of electrolyte. However all the electrolyte concentrations used by Clunie *et al.* and Buscall *et al.* were much below the electrolyte concentrations used in this study and therefore a comparison between these different types of investigation is difficult.

A pattern similar to that shown in fig. 5.9, has been found for the Huggins constant $k_H$ in fig. 3.15. The similarities in the trends obtained with the film thickness and the Huggins constant are obvious. As has been mentioned in section 3.6 $k_H$ is an interaction energy parameter which also contains some micellar size information. The same information can also be obtained from film thickness measurements. Therefore it may be concluded that the liquid film thickness results are consistent with the viscosity results described in chapter 3.

These experimental results of the liquid film thickness measurements in the presence of electrolytes can be explained in terms

of reduction of the solvent quality and by ion absorption. More information on the effect of these electrolytes on the Synperonic surfactants is required to distinguish between the two models.

5.4.2.4 *Influence of temperature*

Since aqueous solutions become poorer solvents for ethoxylated surfactants at higher temperatures it is expected that the film thickness will decrease with increase of temperature. This has in general been found (table 5.6) although the effect is not very large. In the previous chapter, however, it has been shown that the adsorption of the Synperonic NPE 1800 on PS latex and silica increases with increasing temperature. A similar trend for the adsorption of the Synperonic NPE surfactants at the liquid/air interface may be expected. This means that with increasing temperature an increasing amount of surfactant shows a reduction in the liquid film thickness, indicating that a rise in temperature reduces the solvent quality much more than can be deduced from table 5.6 alone.

The minor exceptions of the observed trend result from experimental difficulties with the measurements as could be deduced from the recorded irregular drainage pattern.

Table 5.6 Influence of the temperature on the thickness of equilibrium films stabilized by Synperonic NPE surfactants.

| Surfactant | film thickness (nm) | | |
|---|---|---|---|
| | 288 K | 298 K | 308 K |
| NPE 1800 | 12.5 | 11.6 | 11.4 |
| NPE A | - | 13.9 | 13.6 |
| NPE B | - | 15.7 | (17.0) |
| NPE C | (21.9) | 23.1 | 22.3 |

It can be concluded that the general trend is in agreement with the results of the previous section and strongly suggest that the reduction of the solvent quality is the main factor for the liquid film thickness.

## 5.5 Concluding remarks

Free liquid film thicknesses of Synperonic NP and NPE surfactants have been measured as a function of various parameters. All films were mobile and the film thickness depended to a large extent on the ethoxy chain length. The measured film thicknesses were in good agreement with layer thicknesses obtained from streaming potential measurements, also indicating that the applied optical corrections in the film thicknesses were correct. The film thickness did not change as a function of surfactant concentration in the range studied. From thickness measurements of films stabilized by binary mixtures of surfactants it was demonstrated that fractionation did not occur in the free liquid films.

The film thickness could be interpreted by assuming a simple model in which the ethoxy chain behaves as a terminally anchored chain with dimensions similar to that of a coil trapped in a narrow tube. The experimental results obtained by changing the solvent quality for the ethoxy chain were also consistent with this model.

# 6 STABILITY OF EMULSIONS IN THE PRESENCE OF ELECTROLYTES

## 6.1 Introduction

Chapter 4 dealt with a *reversible* type of instability viz. the flocculation of emulsions. In this chapter the *irreversible* instability due to coalescence will be the main objective.

Destabilisation of the droplets by coalescence in an emulsion is governed by other factors than those which prevail in the emulsification process (Walstra, 1983). At present there is no good theory yet to predict correctly the coalescence of emulsions at rest (Tadros and Vincent, 1983). Coalescence results from rupture of the thin film formed when two approaching droplets come in close contact. When emulsion droplets coalesce immediately after flocculation, the latter process is rate determining and coalescence will be a second order process. On the other hand, if no immediate coalescence occurs after flocculation the coalescence rate will obey first order kinetics. In practice, a first order process is mostly found, which indicates that some time is available to form a thin film of continuous phase between the droplets. It is likely that the stability of this film controls the stability of the emulsion. Although the process of rupture is not yet fully understood, it is likely that rupture of the thin film requires some activation energy. It has been suggested by Vrij and Overbeek (1968) that the growth of small wavelike fluctuations (that are present as a result of thermal motion or external vibrations) is the most important rupture mechanism. The thin film is stable if the waves are damped but rupture will occur if the waves grow. From this rupture theory it follows that instability occurs at low $\gamma$ and with thin films, but if the wavelength of a disturbance is longer than the diameter of the film, the system will be stable. Experimental results show that film rupture indeed occurs frequently whenever the system is instable according to this theory. However, theoretical stability does not always mean actual stability in practice (Walstra, 1984).

Since there is still al lack of good experimental data for understanding the coalescence phenomena, a systematic study of the

destabilisation of emulsions was undertaken. Emphasis was laid on the coalescence of emulsions stabilized by Synperonic NPE 1800, highlighting the role of electrolytes. Coalescence of flocculated and non-flocculated emulsions was studied as a function of time.

## 6.2 Experimental

### 6.2.1 Preparation

As the properties of an emulsion can markedly depend on the method of emulsification, a standard preparation procedure has been adopted, which was similar to that described by Lankveld and Lyklema (1972). A 250 $cm^3$ glass beaker was filled with 60 ml of liquid paraffin. 40 ml of a 3 % (w/w) NPE 1800 solution was then added carefully and the contents of the beaker were emulsified with a type T45 Ultra-Turrax, ex Janke and Kunkel KG Germany. The time of emulsification was 2 minutes, after which the temperature of the emulsion was approximately 345-350 K. Preliminary experiments had shown that increasing the concentration of nonionics and the emulsification time had little or no effect on the particle size distribution of the emulsion obtained. After preparation the emulsion was immediately cooled to room temperature. Finally this stock emulsion was carefully diluted with water or electrolyte solution to a desired volume fraction and electrolyte concentration. Six samples were thus made and the diluted emulsions were stored in duplicate at three different temperatures (298 ± 1 K; 310 ± 1 K and 323 ± 1 K). Deliberately no precautions have been taken to avoid creaming. The preparation of only one stock emulsion was preferred for two reasons. Firstly, the stability behaviour of one and the same emulsion could be studied at different temperatures and, secondly, electrolytes could not interfere with the emulsification process. In this way, flocculation conditions were created only *after* the emulsions were formed.

### 6.2.2 Determination of stability

Since coalescence is the disappearance of the boundary between two droplets, the number of droplets decreases and the average droplet size increases. These two quantities can be used as sui-

table parameters for assessing the stability against coalescence and both can be obtained from a frequency distribution with respect to the diameter (d') of the droplets (Walstra *et al.*, 1969b). The distribution function is called F(d') and the n-th moment of the distribution, $S_n$, is defined by:

$$S_n \equiv \int_o^\infty d'^n f(d')\delta d \qquad (6.1)$$

From the moments of the distribution any average diameter ($d'_{nm}$) and the variation coefficient of the distribution ($c_n$) can be derived:

$$d'_{nm} = \left(\frac{S_n}{S_m}\right)^{\frac{1}{n-m}} \qquad (6.2)$$

and

$$c_n = \left(\frac{S_n S_{n+2}}{S_{n+1}^2} - 1\right)^{\frac{1}{2}} \qquad (6.3)$$

From these equations, the total number of droplets per unit volume $N_t (= S_o)$, the volume-surface average diameter $d'_{vs}$ ($= d'_{32} = S_3/S_2$) and the relative standard deviation of the surface-weighted distribution $C_s (= C_2)$ can be obtained. These parameters are most suitable for the characterization of emulsions (Walstra *et al.*, 1969b).

The size distribution of the emulsions was determined by the Coulter Counter technique (see e.g. fig. 6.1). This method is based upon the registration of voltage pulses, arising when particles pass through a narrow opening across which an electric field is applied. The size of the voltage pulse is proportional to the volume of the passing droplets. By means of a built-in multi-channel analyzer, the cumulative number of pulses above certain preset levels are counted and a cumulative size distribution can be obtained.

A TA II model Counter was used with an orifice of 30 μm. The instrument was calibrated with a homodisperse latex dispersion with particles of 2.04 μm, supplied by Coulter Electronics Ltd. (U.K.).

The total number of droplets in the emulsion and $d'_{vs}$ were measured as a function of time in the following way. After certain time intervals, the emulsions were deflocculated by lowering the temperature. Small samples of emulsion were taken by weight in duplicate after gently redispersing. Immediately after sampling the emulsions were brought back to their original temperature. It was checked that the sampling did not affect the droplet size distribution. The removed samples were diluted 50-100 fold with an aqueous solution of 0.1 % (w/w) polyoxyethylene lauryl ether (Brij 35, ex Atlas Chemicals) to ensure complete deflocculation. These diluted samples were further diluted 1000 fold with Isoton II (ex Coulter Electronics Ltd., U.K.) a dust-free aqueous electrolyte solution, after which the number of droplets was counted.

Although agreement between droplet size distributions obtained by the Coulter Counter technique and other methods such as spectroturbidimetry is reasonably good (Walstra, 1968), some care has to be exercised in the interpretation of the Coulter Counter results. This technique has some limitations which have been extensively discussed by Walstra and Oortwijn (1969a). Generally, the average droplet size measured with the Coulter Counter is somewhat higher

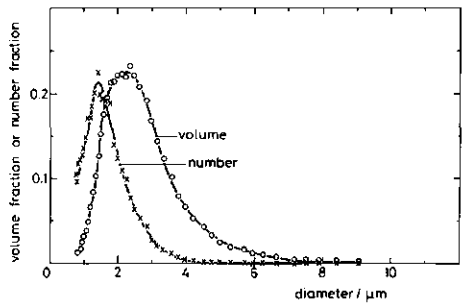


Fig. 6.1 Example of the number and volume frequency of droplets in an oil-in-water emulsion stabilized by Synperonic NPE 1800, obtained with the Coulter Counter ($\phi$ = 0.6, $d_{vs}$ = 2.4 µm and $c_s$ = 0.48).

than the average diameter obtained by e.g. turbidimetry. This discrepancy is greater when the droplets are small because the small droplets are missed by the Coulter Counter (Walstra and Oortwijn, 1969a; Lankveld and Lyklema, 1972; Van Boekel, 1980).

Data obtained with the Coulter Counter have to be statistically corrected for coincidence, i.e. the phenomenon that more than one droplet passes simultaneously through the orifice and gives only one signal. A coincidence correction factor has to be obtained experimentally, since Walstra and Oortwijn (1969a) found the value given in the instruction manual to be approximately half the real value. Results of multiple counts at a series of concentrations are given in fig. 6.2. On the basis of these data a coincidence correction factor of 1.5 times the recommended factor has been chosen. This correction factor was applied to all cumulative numbers of the different channels. As an extra precaution, all measurements were performed with two low concentrations. The inaccuracies in $d'_{vs}$ and $N_t$ determined in this way were always less than 2.5 %. Therefore the average of the values obtained in this way was considered reasonable.

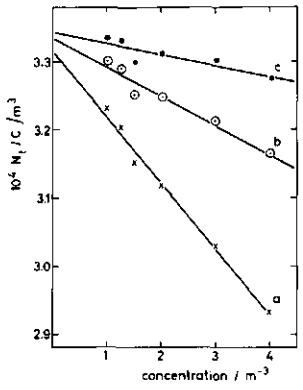


Fig. 6.2 Coincidence correction determined with a 2.04 μm latex (discrimination level 1.6 μm, aperture diameter 30 μm). Curve a - uncorrected; curve b - correction equation $N_t = n + pn^2$ with $p = 0.675 \cdot 10^{-6}$; curve c - similar to b, $p = 1 \cdot 10^{-6}$.

As a check the factor $R_c$ (total dispersed volume obtained from droplet counting divided by the original value) was calculated. For the stock emulsions, immediately after preparation, $R_c$ was nearly always within 5 per cent of the theoretical value ($R_c = 1$). The deviation was larger in the case of unstable emulsions.

## 6.3 Results and discussion

Coalescence can be described as a first order process (Van den Tempel, 1953, 1957; Van Boekel and Walstra, 1981):

$$N_x = N_o \exp(-k_c t) \qquad (6.4)$$

where $N_o$ and $N_x$ are the number of particles at time zero and x, respectively, and $k_c$ is the rate of coalescence. The value of this rate constant can be used as a measure of emulsion stability against coalescence. Usually $k_c \leq 10^{-7}$ $s^{-1}$ is taken as a criterion for stable emulsions and $k_c \geq 10^{-3}$ $s^{-1}$ for unstable emulsions (Van den Tempel, 1953; Van Boekel, 1980). In the latter case, coalescence will be the rate determining process, if the number of droplets is not too small ($N_o > 10^{13}$ $m^{-3}$). Only for very dilute and unstable emulsions a second order process is to be expected (see i.e. Reddy and Fogler, 1980).

The coalescence rate for the emulsions stabilized by Synperonic NPE 1800 was estimated by measuring the number of droplets as a function of time and taking the initial slope from a plot of the logarithm of $N_x$ against the time x (see fig. 6.3).

Values of $k_c$ for emulsions stored at different conditions are tabulated in table 6.1. For $k_c \sim 10^{-7}$ the reproducibility of $k_c$ is about 80%, but it is poorer for lower values of $k_c$. The negative sign for some very small values of $k_c$ must be attributed to an inaccuracy of the method used. The suggestion that the negative values are due to the growth of very small, originally undetected droplets is not very likely, since small droplets are more stable than larger ones. Accepting these inaccuracies the following trends are observed.

In the first place, all emulsions studied are very stable, even if they are flocculated. This implies that a clear distinction

Table 6.1 Coalescence rate $k_c$ for paraffin-oil-in-water emulsions stabilized by Synperonic NPE 1800 in the presence of electrolytes

| Storage Temperature (K) | Volume fraction oil - | Rate of coalescence $k_c$ ($s^{-1}$) | | | |
|---|---|---|---|---|---|
| | | no electrolyte added | 0.4 M $Na_2SO_4$ | 0.4 M $MgSO_4$ | 4 M NaCl |
| 298 | 0.4 | $2.2 \cdot 10^{-10}$ (<c.f.t.) | $-9.1 \cdot 10^{-10}$ (<c.f.t.) | $9.6 \cdot 10^{-10}$ (<c.f.t.) | $6.5 \cdot 10^{-9}$ (<c.f.t.) |
| 298 | 0.2 | $1.7 \cdot 10^{-9}$ (<c.f.t.) | $4.2 \cdot 10^{-9}$ (<c.f.t.) | $5.4 \cdot 10^{-9}$ (<c.f.t.) | $1.5 \cdot 10^{-8}$ (<c.f.t.) |
| 310 | 0.4 | $-1.4 \cdot 10^{-9}$ (<c.f.t.) | $1.7 \cdot 10^{-9}$ (~c.f.t.) | $4.9 \cdot 10^{-9}$ (≦c.f.t.) | $2.8 \cdot 10^{-8}$ (≧c.f.t.) |
| 310 | 0.2 | $-5.0 \cdot 10^{-10}$ (<c.f.t.) | $5.8 \cdot 10^{-9}$ (~c.f.t.) | $7.0 \cdot 10^{-9}$ (≦c.f.t.) | $1.4 \cdot 10^{-7}$ (≧c.f.t.) |
| 323 | 0.4 | $-1.8 \cdot 10^{-9}$ (<c.f.t.) | $4.8 \cdot 10^{-11}$ (>c.f.t.) | $2.3 \cdot 10^{-10}$ (>c.f.t.) | $7.2 \cdot 10^{-8}$ (>c.f.t.) |
| 323 | 0.2 | $2.4 \cdot 10^{-8}$ (<c.f.t.) | $2.9 \cdot 10^{-8}$ (>c.f.t.) | $3.1 \cdot 10^{-8}$ (>c.f.t.) | $7.3 \cdot 10^{-7}$ (>c.f.t.) |
| | | 4 M NaCl | 3.5 M NaCl | 3 M NaCl | |
| 323 | 0.2 | $7.3 \cdot 10^{-7}$ (>c.f.t.) | $4.0 \cdot 10^{-7}$ (>c.f.t.) | $3 \cdot 10^{-7}$ (>c.f.t.) | |
| | | 4 M LiCl | 2 M $CaCl_2$ | 1.4 M $Na_2SO_4$ | |
| 323 | 0.4 | $8.1 \cdot 10^{-9}$ (<c.f.t.) | $5.2 \cdot 10^{-9}$ (<c.f.t.) | | |
| 323 | 0.2 | $2.9 \cdot 10^{-8}$ (<c.f.t.) | $3.0 \cdot 10^{-8}$ (<c.f.t.) | $4.8 \cdot 10^{-6}$ (>c.f.t.) | |
| | | 0.4 M $Na_2SO_4$ | 1 M $Na_2SO_4$ | | |
| 298 | 0.4 | $-9.1 \cdot 10^{-10}$ (<c.f.t.) | $3.7 \cdot 10^{-9}$ (>c.f.t.) | | |
| 310 | 0.4 | $1.7 \cdot 10^{-9}$ (~c.f.t.) | $1.6 \cdot 10^{-8}$ (>c.f.t.) | | |
| 323 | 0.4 | $4.8 \cdot 10^{-11}$ (>c.f.t.) | $7.2 \cdot 10^{-8}$ (>c.f.t.) | | |
| | | 0.68 M $Na_2SO_4$ | | | |
| 298 | 0.5 | $1.2 \cdot 10^{-9}$ (>c.f.t.) | | | |
| 310 | 0.5 | $-2.6 \cdot 10^{-10}$ (>c.f.t.) | | | |
| 323 | 0.5 | $7.4 \cdot 10^{-8}$ (>c.f.t.) | | | |

can be made between the processes of flocculation and coalescence. In many cases this distinction has been confused in the literature (see i.e. Reddy *et al.*, 1981).

In the second place, although all emulsions were very stable, some distinct features emerge from table 6.1. Of the several electrolytes investigated, only NaCl and, to a lesser extent $Na_2SO_4$ at very high concentrations, showed significant coalescence after several weeks. Since NaCl did not show any exceptional behaviour with respect to flocculation, this is another indication that flocculation and coalescence are different processes.

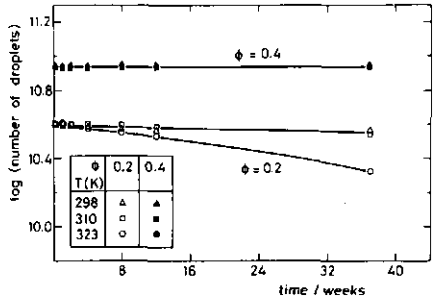


Fig. 6.3 Variation of the number of emulsion droplets in the presence of 0.4 M $Na_2SO_4$ ($d'_{vs}$ = 2.5μm)

In the third place, dilute emulsions coalesce much faster than more concentrated ones (see table 6.1 and fig. 6.3). The reverse was expected because of the increased stress on the droplets which is a linear function of the thickness of the cream layer. Since all emulsions were prepared from the same stock sample, and creaming was relatively fast, it is highly unlikely that the increased coalescence in the dilute emulsion is due to a more rapid creaming process. Another difference between the dilute and concentrated emulsions was the final bulk surfactant concentration, which increased with increasing volume fraction of oil. In order to eliminate any effect from this difference the experiment was repeated while keeping the bulk surfactant concentration constant and measuring the time after which the emulsion was broken in the presence

of 4 M NaCl at 323 K. Again it was observed that dilute emulsions coalesce much faster than more concentrated ones, irrespective of the final bulk surfactant concentration.

In addition several experiments have been carried out to investigate the effects of ullage and creaming at various volume fractions (at 323 K in the presence of 4 M NaCl). Emulsions which were stored in partially filled containers without preventing creaming coalesced at a faster rate than those placed in more filled vessels. Similar results have been obtained when the emulsions were prepared under nitrogen and stored under nitrogen, indicating that this phenomenon was not due to oxidation of the surfactant.

Emulsion stability was also investigated when creaming was prevented. This was achieved by rotating the emulsions slowly. If nearly all air was excluded, the investigated emulsions were more stable than when they were left to cream. Moreover, it was noticed that under rotating conditions concentrated emulsions coalesced faster than those with a small volume fraction. However, in the presence of air all rotated emulsions coalesced at a much faster rate than when left to stand. The last mentioned phenomenon can be attributed to the tendency of the oil to spread over the air-water interface (Mulder and Walstra, 1974).

An adequate explanation could not be offered for the difference in coalescence rate as a function of volume fraction of the oil phase and the effect of ullage upon the stability.

Accepting some unclear trends in the coalescence rate, the emulsion stability as a function of electrolyte concentration and temperature variation may be considered as being governed by the rupture of the thin film between two droplets. In that case emulsion stability criteria may be obtained by applying the film rupture theory of Vrij and Overbeek (1968). Taking only the Van-der Waals-attraction between the droplets into account, these authors derived the following equation for the critical wave length $\Lambda_{crit}$:

$$\Lambda_{crit} = 2\pi \sqrt{\frac{\pi\gamma h^4}{A_{11}}} \qquad (6.5)$$

where $\gamma$ and $A_{11}$ have their usual meaning and h is the thickness of the liquid film between two emulsion droplets. Above this critical wavelength the surface fluctuations tend to grow spontaneously in amplitude, leading to film rupture or to stabilization as a black film (see previous chapter). However, if this critical wave length exceeds the diameter of the film, the film will be stable. Taking the geometric restrictions of the films between droplets in an emulsion into consideration and on the basis of the above rupture theory an emulsion stability criterion can be obtained (Walstra, 1984). Emulsions are stable if:

$$h > \sqrt[3]{\frac{A_{11} d'_{vs}}{2\pi\gamma}} \qquad (6.6)$$

From equation 6.6 it follows that generally a smaller film has greater stability, meaning that smaller droplets are more stable than larger ones under otherwise identical conditions. It follows also from this criterion that lowering of the interfacial tension ($\gamma$) would lead to a less stable system.

Applying this stability criterion to the system used in this study some trends can be observed. Surfactants with a long ethoxy tail and hence a thick liquid film impart good stability (see table 2.5). The other surfactants of the Synperonic NPE series are therefore expected to give a better stability than Synperonic NPE 1800, whereas lowering of the ethoxy chain length will result in less stability. However, as emulsion stability as a function of the ethoxy chain length of the surfactant was not the aim of the present study, this trend was not investigated.

Considering these trends observed for the liquid film thickness between two emulsion droplets (h) the following can be noted.

In the first place, the liquid film thickness was reduced with increasing temperature (see previous chapter). This implies that the emulsion stability will decrease with increasing temperature. Experimentally this trend was observed for emulsions in the presence of 4 M NaCl and also to some extent in the presence of 0.4 M $Na_2SO_4$ (see table 6.1). Emulsion instability will also be enhanced by the small lowering of the interfacial tension due to

the increase of temperature, which has been shown to occur by Van den Boomgaard *et al.* (1983).

In the second place, a reduction of the film thickness due to electrolyte was found above 0.1 M $Na_2SO_4$ and above 2 M NaCl (see fig. 5.9). This reduction also corresponds with an increase in the coalescence rate for emulsions as a function of electrolyte concentration (see table 6.1).

From the above results it can be concluded that the rupture theory of Vrij and Overbeek properly predicts the influences of electrolytes and temperature changes on the coalescence of emulsions stabilized by Synperonic NPE 1800. However, the differences in coalescence rate as a function of oil volume fraction could not be explained by this theory.

## 6.4 Concluding remarks

The stability against coalescence of emulsions stabilized by Synperonic NPE 1800 in the presence of electrolytes has been studied. A clear distinction could be made between the processes of flocculation and coalescence. All emulsions studied were very stable according to criteria given in the literature, only in the course of several weeks some coalescence could be observed. The trends of these coalescence phenomena as a function of electrolyte concentration and temperature, but not those observed with the oil volume fraction, could be described with the film rupture theory of Vrij and Overbeek.

# 7 THE ROLE OF ELECTROLYTES IN THE FLOCCULATION AND COALESCENCE OF EMULSIONS

The present investigation has dealt with factors governing the colloidal stability of emulsions under conditions where the DLVO-theory is inapplicable, namely in solutions which contained a very high concentration of electrolytes. Particular attention was paid to the nature of the electrolyte and experiments were carried out at various temperatures. Under these conditions stability can be obtained by various nonionic surfactants. One of the main issues of this study was thus defined as the behaviour of these surfactants in electrolyte solutions.

Destabilization of an emulsion can be obtained by flocculation or coalescence. The latter process is typical for emulsions. It is the aggregation of droplets with the disappearance of boundaries separating them. Flocculation is only aggregation of particles and is therefore a phenomenon that emulsion droplets have in common with particles of other matter, stabilized by the same surfactant. For this reason a close analogy between emulsions, latices and various solid dispersions, stabilized by the same surfactant, was expected and found with respect to the stability against electrolytes.

It was anticipated that coalescence and flocculation would depend in a different way on the nature and concentration of electrolytes. This difference has indeed been found.

In order to study flocculation it was advantageous to have a closer look at the interaction between various particles covered with the same surfactant, micelles of this surfactant and thin films stabilized by this surfactant. With respect to the effect of electrolytes the following common trends were found.

Thin film thickness passes through a maximum as a function of the ionic strength (see fig. 5.9). A similar pattern was obtained for the Huggins constant $k_H$, as shown in fig. 3.15. As has already been mentioned this Huggins constant also contains some information about the micellar size. The similarities in the trends are obvious. The occurrence of this maximum in the film thickness and

in the Huggins constant as a function of ionic strength indicates that there are two counteracting effects. For the film thickness these effects could be attributed to an increase of adsorption of surfactants and reduction of the extension of the ethoxy chains. Both effects are due to a decrease of solvent quality with an increase of electrolyte concentration. However, the influence of the electrolytes on the Huggins constant is more complicated. More information on the effect of electrolytes on the size and shape of the micelles is needed to eludicate these two opposing trends.

A close relationship was found between the adsorbed amount and the critical flocculation temperature as a function of nature and concentration of electrolyte (see e.g. fig. 4.1 and fig. 4.11).

It was established that the ethylene oxide moiety of the surfactant is primarily responsible for all these types of interactions. The conclusion is that these features have a common principle which must be related to the solution properties of the ethylene oxide part of the surfactant. Attempts to analyse these properties in detail led to the suggestion of measuring the density and heat capacity of well defined ethoxylated surfactants with a relatively high c.m.c. value as a function of nature and concentration of electrolyte and temperature. Applying dynamic light scattering to micelles of these surfactants under similar conditions would also be valuable.

As mentioned before the coalescence behaviour followed entirely different laws. Coalescence also depends on the nature of electrolytes but in a different fashion. Unfortunately the emulsions studied were too stable to study this in great detail. At any rate there are reasons to suppose that the electrolyte effect regarded the hydrophobic, rather than the hydrophilic moiety of the surfactant. Part of the coalescence trends could at least qualitatively be explained by the Vrij and Overbeek theory, which attributed coalescence to the growth of thermal fluctuations in the liquid film separating neighbouring droplets. However, the effect of the volume fraction of the oil upon coalescence remained unexplained and requires further investigation. These investigations should be performed with less stable emulsion systems and emphasis should

also be placed on the distribution of the stabilizer between the two phases.

The final conclusion, obtained with the present system is that the influences of electrolytes on flocculation and coalescence obey different laws.

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SUMMARY

The objective of this study was to investigate the effect of high electrolyte concentrations on the stability of oil-in-water-emulsions stabilized by nonionic surfactants.

In chapter 1 several stability mechanisms are briefly outlined and the distinction between coalescence and flocculation of an emulsion is explained.

The structural characterization of the nonionic surfactants used (Synperonic NPE series) is described in chapter 2. These surfactants consist of a hydrophobic nonylphenol part, a less hydrophobic propylene oxide part (PO) and a hydrophilic ethylene oxide moiety (EO). Various samples differing with respect to the length of the EO part have been studied. Consistent results for the molecular masses have been obtained by pmr- and uv-spectroscopy. It has been demonstrated that the hydrophobic nonyl group of the surfactant is branched in different ways but there is no significant preference for any of the aliphatic nonyl isomers in the ethoxylation process.

In chapter 3 attention is paid to the properties of surfactant solutions by studying the surface- and interfacial tension, density, heat capacity, light scattering and viscosity. It was found that Synperonic NPE surfactant solutions have properties similar to other ethoxylated surfactant solutions and that the solvent quality of the EO-moiety plays the main role in the solution behaviour of NPE surfactants. With respect to the effect of concentrated electrolytes it was established that there are two opposing trends which lead to a maximum in the micelle interaction coefficient as a function of salt concentration.

Chapter 4 is devoted to the adsorption behaviour of Synperonic surfactants and to the flocculation of dispersions stabilized with these surfactants. The adsorption was found to depend on the nature of the adsorbent, which had consequences for the stability of the dispersions. Polystyrene latices and emulsions could be stabilized with Synperonic NPE surfactants in electrolyte solutions, whereas

pyrogenic silica could not. The PS latex flocculated under theta conditions for poly ethylene oxide indicating that the ethylene oxide moieties of the adsorbed surfactants protrude into the aqueous solution.

Free liquid film thickness measurements are treated in chapter 5. For comparison purposes also a number of experiments has been carried out with Synperonic NP, a surfactant similar to NPE but without the propylene fraction. The measured film thicknesses were in good agreement with layer thicknesses obtained from the reduction in the streaming potential in a narrow capillary. This agreement supports the correctness of the two different techniques. The film thickness depended strongly on the ethoxy chain length and did not change with increase of surfactant concentration in the range studied. From thickness measurements of films stabilized by binary mixtures of surfactants it was demonstrated that fractionation did not occur in the free liquid films. The film thickness could be analyzed using a simple model in which the ethoxy chain behaved as a terminally adsorbed chain with dimensions similar to a coil trapped in a tube. The effect of electrolytes obeyed laws similar to those observed in chapter 3 and was entirely attributable to the interaction of the EO parts of the molecule.

Chapter 6 deals with the stability against coalescence of emulsions stabilized by Synperonic NPE 1800 in the presence of electrolytes. All emulsions studied were very stable according to criteria given in the literature, only in the course of several weeks some coalescence could be observed. The trend as a function of electrolyte concentration and temperature could be described with the film rupture theory of Vrij and Overbeek, but the observed effect of the oil volume fraction upon coalescence could not be explained with this theory.

Finally in chapter 7 the conclusion is obtained that with the present system the influence of electrolytes on the flocculation and coalescence are entirely different processes. Flocculation is due to interaction between the ethylene oxide moieties; with respect to this phenomenon the effect of electrolytes is similar to that observed in solutions of the surfactants and in the thin films.

SAMENVATTING

Dit proefschrift heeft tot onderwerp de invloed van elektrolieten op de stabiliteit van emulsies. Voor de duidelijkheid zal eerst kort worden ingegaan op enkele kolloïdchemische begrippen.

De *kolloïdchemie* is een tak van wetenschap die het gedrag van net niet met het blote oog waarneembare deeltjes, die *gedispergeerd* (= fijn verdeeld) zijn in een andere stof bestudeert. Zowel die stof als de deeltjes zelf kunnen vast, vloeibaar of gasvormig zijn. Van deze vorm is de naamgeving van dergelijke *dispersies* mede afhankelijk.

Een dispersie van kleine vaste deeltjes in een vloeistof wordt een *suspensie* genoemd. Voorbeelden hiervan in het dagelijks leven zijn verf en inkt, maar ook rivierwater waarin kleideeltjes zweven zou men een suspensie kunnen noemen.

Zijn de kleine deeltjes vloeibaar, dus eigenlijk druppeltjes en verdeeld in een vloeistof, dan spreekt men van een *emulsie*. Een voorbeeld van een emulsie van vetdruppels in water is melk.

Dit onderscheid tussen suspensie en emulsie doet misschien kunstmatig aan, wanneer men bedenkt dat melk die in de koelkast bewaard wordt als een suspensie moet worden beschouwd omdat de vetdruppels dan gestold zijn. Toch is dit onderscheid in kolloïdchemische zin belangrijk.

Wanneer gedispergeerde deeltjes makkelijk samenklonteren (= *vlokken*) of in geval van druppels zelfs kunnen samenvloeien (= *koalesceren*) noemt men de dispersie *niet-stabiel*. Tussen deze twee vormen van instabiliteit kan onderscheid gemaakt worden: bij vlokking klonteren de deeltjes (vaste deeltjes òf druppeltjes) samen zonder dat daarbij iets aan de deeltjes zelf verandert, terwijl bij koalescentie er na de samenklontering wel verandering in de deeltjes plaats vindt: ze vloeien samen tot een groter deeltje.

De *stabiliteit* van een dispersie kan bijvoorbeeld ontleend worden aan lading op de deeltjes (kleideeltjes) of door zogenaamde stabilisatoren, zoals eiwitten, polymeren of zepen (bv. voedselprodukten, vloeibare wasmiddelen, verf, e.d.). Deeltjes met gelijke lading

zullen elkaar afstoten en dus niet zo gemakkelijk samenklonteren. Eiwitten en dergelijke zullen zich in meer of mindere mate aan deeltjes hechten, waardoor deze evenmin met elkaar in aanraking kunnen komen.

In sommige gevallen kan goed voorspeld worden hoe stabiel een dispersie zal zijn. De DLVO-theorie, die met name de stabilisatie door lading goed kan beschrijven, voorspelt onder andere dat in aanwezigheid van *elektrolieten* (deze bevatten ionen die eveneens een lading hebben) de stabiliteit van een dispersie minder kan worden of helemaal kan verdwijnen. Toch zijn er vele dispersies die stabiel zijn ondanks de aanwezigheid van grote hoeveelheden elektrolieten. Een biologisch voorbeeld hiervan vormen bacterieën die in de Dode Zee voorkomen. Er moeten dus dan andere stabilisatiefaktoren dan de in de DLVO-theorie beschouwde, in het spel zijn.

De al eerder genoemde stabilisatoren kunnen eveneens worden beïnvloed door grote hoeveelheden elektrolieten; hoe dit precies gebeurt is nog niet volledig bekend. Aangezien dit toch van zeer praktisch belang kan zijn (bijvoorbeeld in de bestrijding van olievlekken op zee) wordt hiernaar intensief onderzoek gedaan. Ook in dit proefschrift wordt getracht hieraan een bijdrage te leveren. Hiervoor is een modelstudie verricht aan emulsies, gestabiliseerd door een stof (nl. Synperonic NPE 1800) die de werking heeft van een zeep, maar ook andere eigenschappen vertoont. In deze studie is vooral de nadruk gelegd op de stabiliteit van emulsies in aanwezigheid van elektrolieten.

De opzet van dit proefschrift wordt beschreven in *hoofdstuk 1*. Omdat weinig bekend was over het gedrag van de stabilisatoren zelf werd daar eerst enig onderzoek naar gedaan (hoofdstuk 3). Verder wordt de nadruk gelegd op de stabiliteit van de emulsies in aan- en afwezigheid van elektrolieten (hoofdstukken 4 en 6).

De chemische struktuur van de stabilisator, Synperonic NPE 1800 en hieraan verwante stoffen (Synperonics NPE en NP) komt aan bod in *hoofdstuk 2*. Hierin wordt verder beschreven hoe deze stoffen gemaakt worden en tevens op welke verschillende wijzen deze gekarakteriseerd kunnen worden. Gebleken is dat alle gebruikte stabilisatoren enige variaties vertonen.

In *hoofdstuk 3* wordt ingegaan op de eigenschappen die de stabilisatoren in water, al dan niet in aanwezigheid van elektrolieten, blijken te bezitten. Bij welke koncentratie de in water opgeloste stabilisatoren aggregeren en in welke mate, werd bestudeerd bij verschillende temperaturen en in aanwezigheid van elektrolieten. Daarvoor werden verschillende technieken gebruikt zoals metingen van de oppervlakte-en grensvlakspanning, dichtheid, warmtekapaciteit, lichtverstrooiing en viskosimetrie. Deze laatste techniek is ook gebruikt voor molekulen die opgebouwd zijn uit slechts dat gedeelte van de stabilisator dat verantwoordelijk gehouden wordt voor de stabiliserende werking (PEO-moleculen).

De *adsorptie* (= ophoping) en het gedrag van de stabilisator aan een *grensvlak* (= de buitenkant van de deeltjes) wordt beschreven in *hoofdstuk 4*. Aangezien het niet goed mogelijk was deze verschijnselen op een eenvoudige wijze aan emulsies te bestuderen, werden deze ook aan twee andere dispersies (polystyreen latex en silica suspensies) onderzocht. Dit gaf tevens de gelegenheid het adsorptie-gedrag aan verschillende soorten grensvlakken te vergelijken. De adsorptie van de stabilisator aan het water-polystyreenlatex grensvlak en aan het water-silica grensvlak bleek nagenoeg gelijk te zijn. In aanwezigheid van elektrolieten bleek de stabiliserende werking bij beide suspensies echter totaal verschillend te zijn.

Het stabiliserend gedrag werd bestudeerd door middel van *vlokmetingen*. Deze werden voornamelijk uitgevoerd aan polystyreenlatex suspensies met daarop geadsorbeerd de stabilisator, omdat deze metingen eenvoudiger uit te voeren zijn, en omdat het vlokgedrag daarvan hetzelfde bleek te zijn als dat van de emulsies bij gebruik van dezelfde stabilisator. Uit deze vlokmetingen bleek dat de stabiliteit van de dispersies verandert bij een bepaalde elektroliet-koncentratie (= kritische elektroliet-koncentratie) en bij een bepaalde temperatuur (= kritische temperatuur). Deze waarden komen nagenoeg overeen met kritische waarden die in de literatuur beschreven staan voor PEO-moleculen in oplossing. De eigenschappen van de silica suspensies met de geadsorbeerde stabilisator bleken totaal anders te zijn. Dit zou erop kunnen wijzen dat het adsorptiemechanisme verschillend zou kunnen zijn, maar dit kon niet aan-

nemelijk gemaakt worden. De adsorptie resultaten zelf duiden eerder op het tegendeel.

Met lichtreflektie werd de dikte van *vliesjes* van de in water opgeloste stabilisator in lucht gemeten. (Een vliesje bestaat als het ware uit een laagje water met aan weerskanten stabilisator.) Deze vliesmetingen worden behandeld in *hoofdstuk 5*. De vliesdikte bleek afhankelijk te zijn van de lengte van het stabilisator-molecuul. De gevonden vliesdiktes komen zeer goed overeen met elektrokinetische dikte metingen. De vliesdikte blijkt onafhankelijk te zijn van de stabilisatorkoncentratie, maar wel afhankelijk van de temperatuur en van de elektrolietkoncentratie. Deze laatste effekten komen overeen met metingen aan de stabilisator in oplossing, zoals beschreven in hoofdstuk 3. Hieruit kan gekonkludeerd worden dat de invloed van elektrolieten op de stabiliteit van het systeem voornamelijk moet worden toegeschreven aan het gedrag van gedeelten van de stabilisator die in de oplossing steken.

In *hoofdstuk 6* is de *koalescentie* van de emulsies beschreven. Uit de metingen blijkt dat de emulsies zeer stabiel zijn ook als ze in gevlokte toestand gebracht worden. Koalescentie trad slecht op onder extreme omstandigheden (hoge temperatuur en hoge elektrolietkoncentraties). Een deel van de tendensen die gevonden werden met de koalescentie, kon redelijk beschreven worden met een theorie die het breekgedrag van dunne vliezen voorspelt.

Tenslotte wordt in *hoofdstuk 7* gekonkludeerd dat de koalescentie en vlokking verschillende processen zijn. Dit blijkt niet alleen uit de kinetiek van de processen maar ook uit de invloed van elektrolieten: vlokking en koalescentie zijn beide gevoelig voor de koncentratie en het soort elektroliet, maar de wijze waarop ze hiervan afhankelijk zijn verschilt duidelijk.

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CURRICULUM VITAE

De auteur werd geboren op 2 januari 1953 te Rotterdam. Hij haalde in 1971 het gymnasium β diploma aan het Libanon Lyceum te Rotterdam, en begon in hetzelfde jaar met de studie aan de Landbouwhogeschool te Wageningen. In januari 1976 werd het kandidaatsexamen Moleculaire Wetenschappen (chemische oriëntatie) afgelegd, en in maart 1979 werd het doctoraal diploma behaald met als hoofdvakken Kolloidchemie en Moleculaire Fysica en als bijvak Wiskunde. Vanaf mei 1979 tot november 1982 was hij in tijdelijke dienst van de Landbouwhogeschool op het laboratorium van Fysische en Kolloidchemie, waar het in dit proefschrift beschreven onderzoek is uitgevoerd. Tijdens dit dienstverband werd gedurende een jaar onderzoek verricht in het laboratorium van ICI-Plant Protection Division te Engeland.

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